Reval PET

Centre Català del Plàstic

UNIVERSITAT POLITÈCNICA DE CATALUNYA BARCELONATECH

eplascom Plásticos y Composites Ecológicos

Projet cofinancé par le Fonds Européen de Développement Régional

Interreg POCTEFA

UNIÓN EUROPEA UNION EUROPÉENNE

# Action 4.
# Scaling-up and Life Cycle Assessment (LCA)

*4.1. Scaling-up*

**Orlando SANTANA PÉREZ**
CCP-UPC Characterization and fracture coordinator.

Magali KLOTZ
Ing. Msc. Material Science and Engineering form EEIGM – UPC.

# Scaling up: Phases

***Objective:*** ***Compounding at pre-industrial level of selected blend composition: rPP/rPET-O: 80/20 with and without 5 % w/w of additional $TiO_2$.***

**Phase 1** "Raw" ***rPET-O*** homogenization

Looking for best processing conditions in order to:

- ✓ Minimize additional degradation of ***rPET-O***
- ✓ Best mechanical properties balance

Flakes

Pellets

**Phase 2** Blends preparation in pre-industrial scale compounding process

- ✓ Selected compostion: rPET-O/rPP: 20/80 + 5 %w/w $TiO_2$
- ✓ Processing conditions that reduce the risk of degradation of the rPP phase.
- ✓ Enough amount to be processed by Injection moulding to obtain selected prototypes (30 kg)

**Phase 3** Blends quality assessment

- ✓ Generation of a technical data sheet for processing.
- ✓ Verification of mechanical properties of the "pre-industrial" material prepared.

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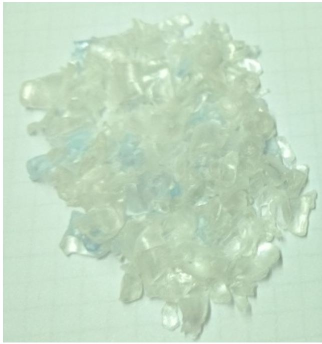
# Phase 1: "Raw" rPET-O homogenization

Determination of Processing window for ***rPET-O*** homogenization and subsequent blending with ***rPP***.

- ✓ Minimize additional degradation of ***rPET-O***
- ✓ Best mechanical properties balance
- ✓ Evaluation of $TiO_2$ effect in this process.

**Control raw material:**
rPET-T flakes
(transparents bottles)



**3 extrusion conditions to explore**

| Code | Temperature profile Z1/…./Z7 (die) (ºC) | Screw rotation speed (RPM) |
|---|---|---|
| C-1 | 200/240/255/260/265/<u>270/270</u> | 130 |
| C-2 | 190/230/245/250/255/<u>260/260</u> | 80 |
| C-3 | 180/215/235/235/240/<u>245/245</u> | 80 |

Commonly used for PET

Based on melting peak temperature (DSC).

**RevalPET raw material:**
rPET-O flakes
(opaque bottles)

Homogenization at the extrusion condition with less degradation effect.

# Phase 1: “Raw” rPET-O homogenization

**Collin® twin screw extruder**
(7 heating zones, L/D =36, D: 25 mm)

**+ 3 vertical roll calendering**
**(ϕ = 70 mm)**
**Collin® Teachline CR72T**

Solid crystallized Dried **flakes**
(dw: -40ºC, 120ºC/4h)

***Homegeneization + Pelletizing***
***(5 kg)***

3 processing conditions

***IV determination***

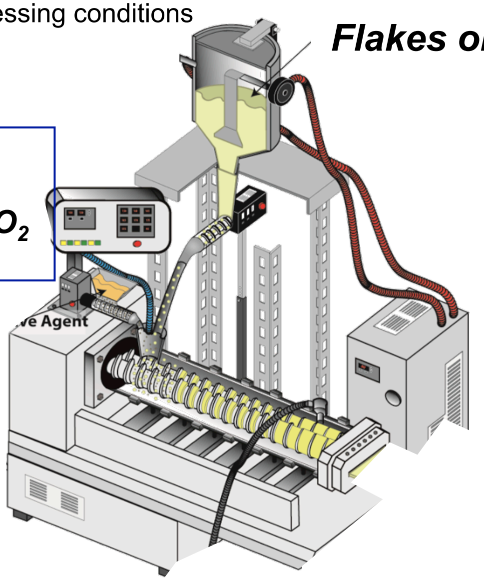
***Determination of $TiO_2$ content***

Pellets Recrystallization (90ºC/4h)
+
Drying
(dw: -40ºC, 120ºC/4h)

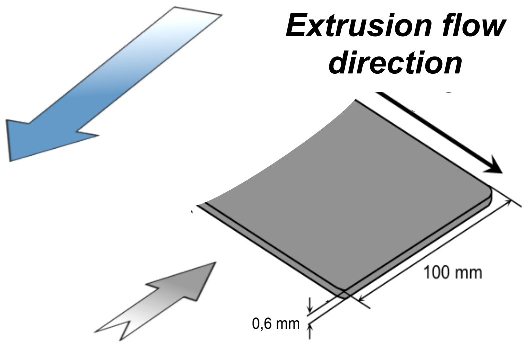
**Extrusion-calendering**
*(20 to 30 m)*

Profile temperature: [180-245ºC]
55 RPM ($t_{residence}$= 4 min)
Chilling rolls: 50ºC / 2 RPM

***Flakes or pellets***




***Extrusion flow direction***




***IV determination***

***Tensile tests*** @ 25ºC

**Tearing behaviour *(EWF)*** @ 25ºC

***Fractographic analysis***

(SEM observations)

# Phase 1: “Raw” rPET-O homogenization

***IV Determination: Mw estimation***

**Methodology:** ASTM D4603 -03
**Equipment:** Ubbelohde capilar viscosimeter Type 1B
**Solvent:** Phenol/1,1,2,2-tetracloroethane: 60/40 w/w.
**Temperature**: 30ºC

| | | Homogenized pellets | |
|---|---|---|---|
| Material | Processing | IV (dL/g) | Mw (kDa) |
| ***r-PET-T*** | **NP** | 0,786 | 52,4 |
| | **C-1** | 0,697 **(-11%)** | 43,5 **(-17%)** |
| | **C-2** | 0,683 **(-13%)** | 42,2 **(-19%)** |
| | **C-3** | 0,712 **(-9%)** | 45,0 **(-14%)** |

**Accepted IV decrease of 5 % ⇒ Loss in Mw < 10%**

| | | |
|---|---|---|
| **C-3** | **180/215/235/235/240/245/245** | **80** |

# Phase 1: “Raw” rPET-O homogenization

***$TiO_2$ content determination***

**Methodolgy:** ISO 3451-1 (Method A)
**Drying condition:** 120ºC/ 1h15min /vacuum oven
**Calcination temperature:** 1200ºC (oven)/3h.
**Nº of samples**: 5
**Weigth of samples:** 10 g.

**Initial burning**

**Calcination in oven**
(1200ºC / 3h)

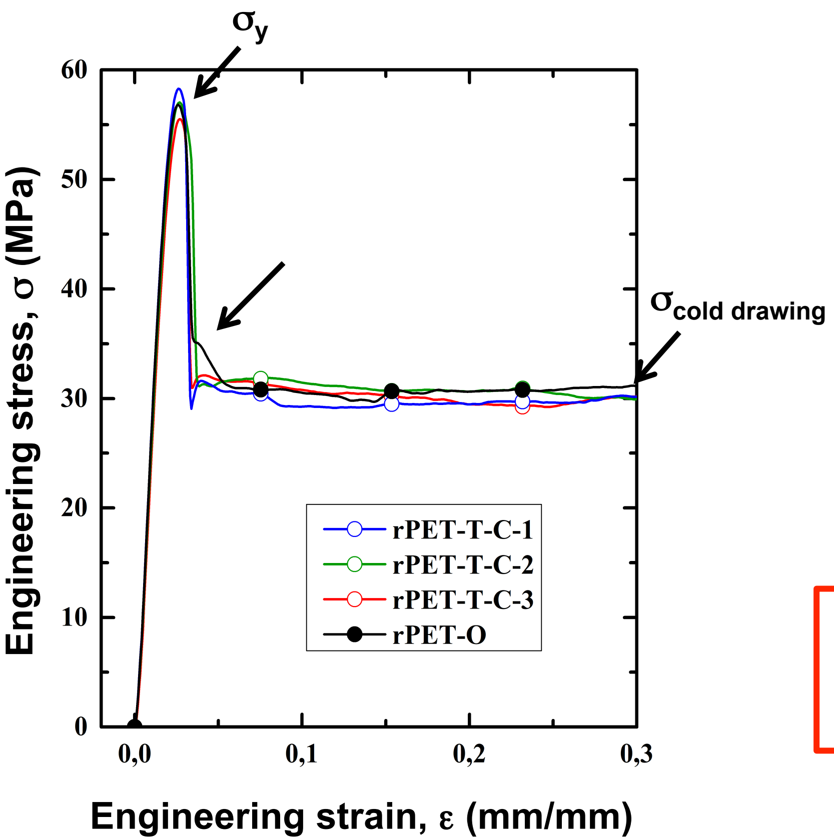
**After oven calcination**

**2,4% (± 0,3) w/w**

# Phase 1: “Raw” rPET-O homogenization

***Tensile tests:***

**Methodology:** ISO 527 – samples type 4 (flow direction)
**Equipment:** Universal testing machine GALDABINI 2500 + Videoextensometer MITRON OS-65D
**Velocity:** 20 mm.min$^{-1}$
**Temperature:** 18ºC ± 2ºC

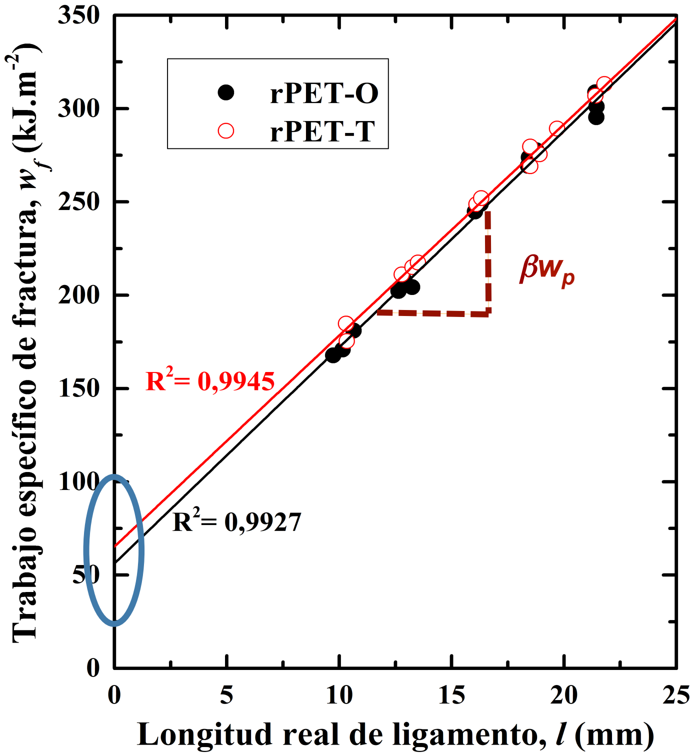



| | Material | | | |
|---|---|---|---|---|
| | *rPET-T* | | | *rPET-O* |
| **Parameter** | **C-1** | **C-2** | **C-3** | **C-3** |
| **$E$ (GPa) (% error)** | 2,1 (4,5%) | 2,09 (2,6%) | 2,2 (4,5%) | 2,20 (1,6%) |
| **$\sigma_y$ (MPa) (% error)** | 59 (1,7%) | 56,9 (1,6%) | 57,0 (0,2%) | 57,4 (0,7%) |
| **$\sigma_{cold\ drawing}$ (MPa) (% error)** | 32 (4,7%) | 32 (3,5%) | 30,9 (2%) | 31,7 (1,3%) |
| **$\varepsilon_{ruptura}$ (mm/mm) (% error)** | 1,9 (18,4%) | 2,0 (23%) | 2,6 (15%) | 2,0 (6%) |

# Phase 1: “Raw” rPET-O homogenization

***Tearing behavior (Slow crack propagation): Specific work of fracture:***

**Methodology: ESIS-TC4**
**Equipment:** Universal testing machine GALDABINI + viedoextensometer MITRON OS 65D
**Velocity:** 10 mm.min$^{-1}$
**Temperature:** 18ºC ± 2ºC
**Sample geometry:** DDENT
**Nº of tested samples**: 15
(3 replicates at 5 ligament length, *l*)




| Material | $w_e$ (kJ.m$^{-2}$) | $\beta w_p$ (MJ.m$^{-3}$) | $\beta$ x 10$^{-2}$ | $w_p$ (MJ.m$^{-3}$) |
|---|---|---|---|---|
| ***rPET-T*** | 65 ± 4 | 11,3 ± 0,2 | 10,1 ± 0,4 | 112 ± 5 |
| ***rPET-O*** | 56 ± 4 | 11,6 ± 0,3 | 8,6 ± 0,3 | 135 ± 8 |
| **SP04[2]** | 56 ± 7 | 11,1 ± 0,5 | 11,6 ± 0,2 | 96 ± 6 |

[2] A. Al-Jabareen, O. O. Santana et al. *J. Mater. Sci.*, **45**(11), 2907-2915 (2010).

$TiO_2$ slightly decrease the $w_e$ (onset of crack propagation) without modification of $\beta w_p$ (crack propatation resistence).

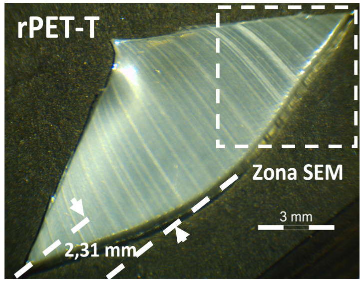
The addition of TiO2 decreases the size of the outter process zone (outside the plane of crack propagation) associated with plastic damage (energy dissipation) during propagation (decrease of $\beta$)

⇓

“nucleating effect” of $TiO_2$ at the test temperature (20 °C) promoting deformation-induced crystallization.

# Phase 1: “Raw” rPET-O homogenization

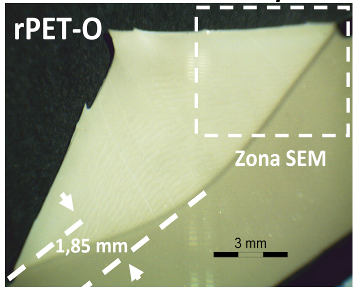
$w_p$ = 112 ± 5 MJ.m$^{-3}$

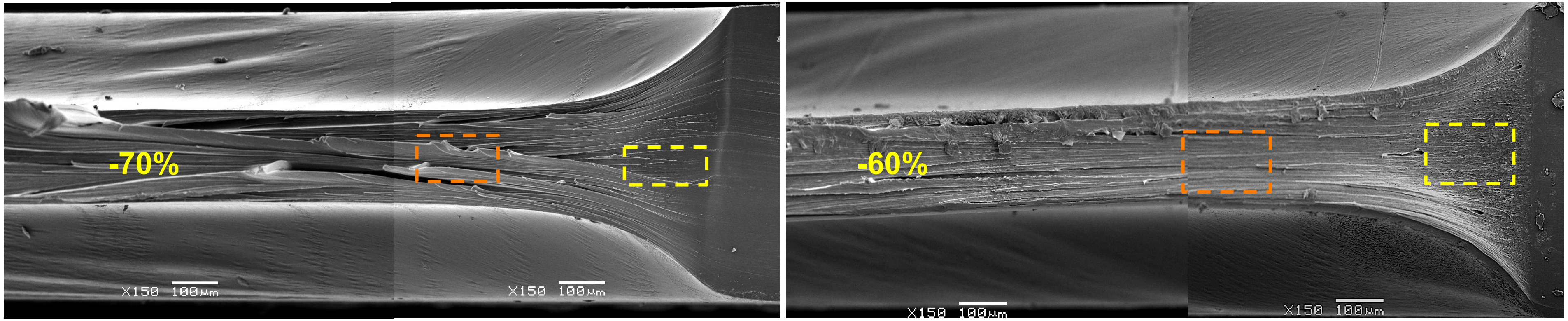



***Fractography***

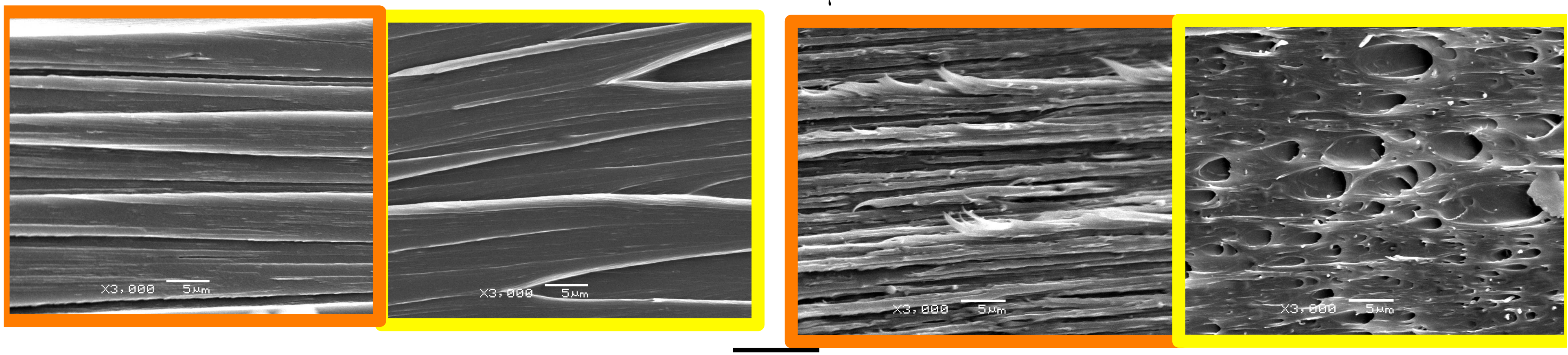
**Equipment:** SEM JSM-5610 (JEOL)
**Conditions:** Vacuum- 10kV
**Samples:** DDENT tests surfaces, covered with Au/Pd.

$w_p$ = 135 ± 8 MJ.m$^{-3}$



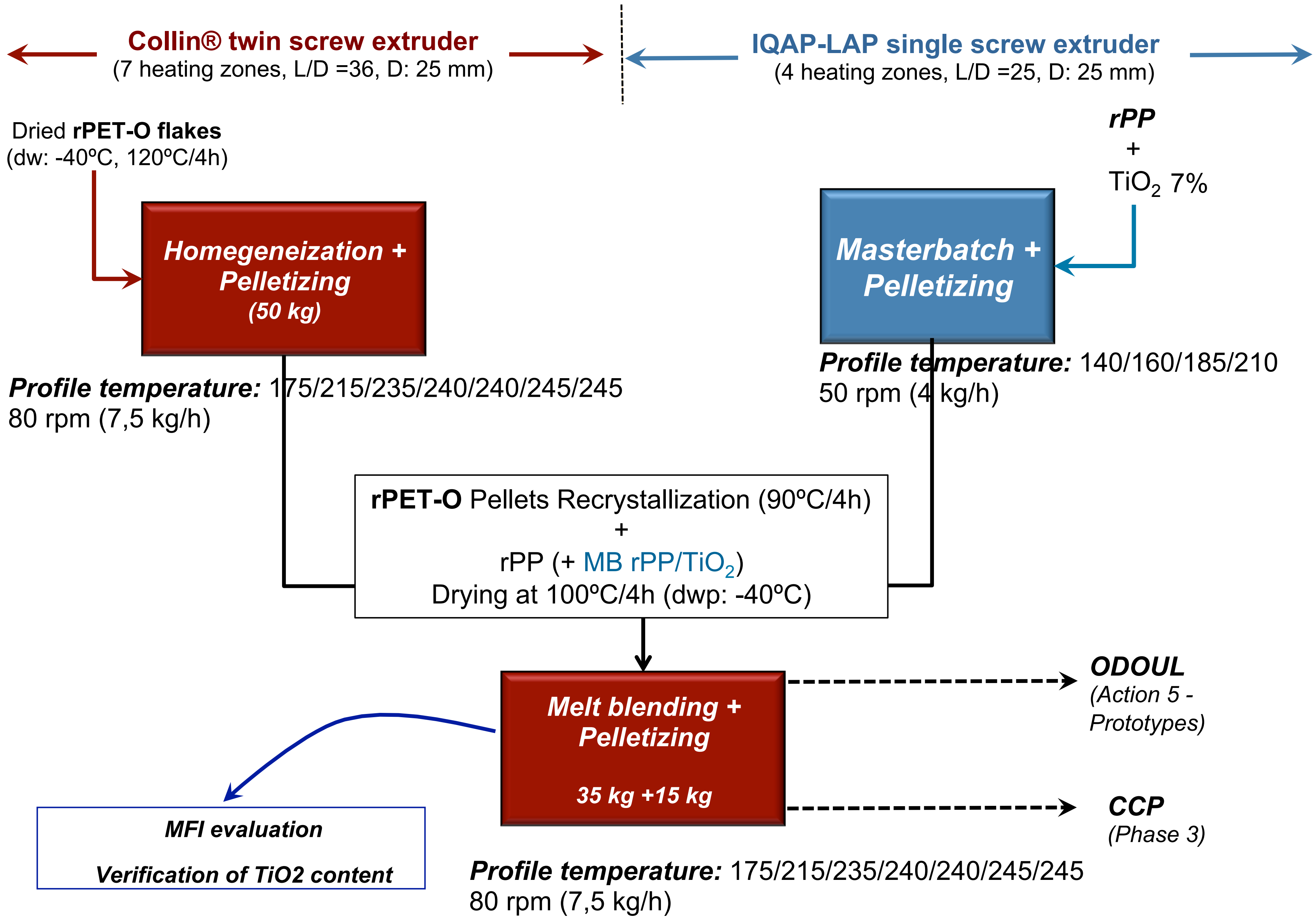




200 μm




10 μm

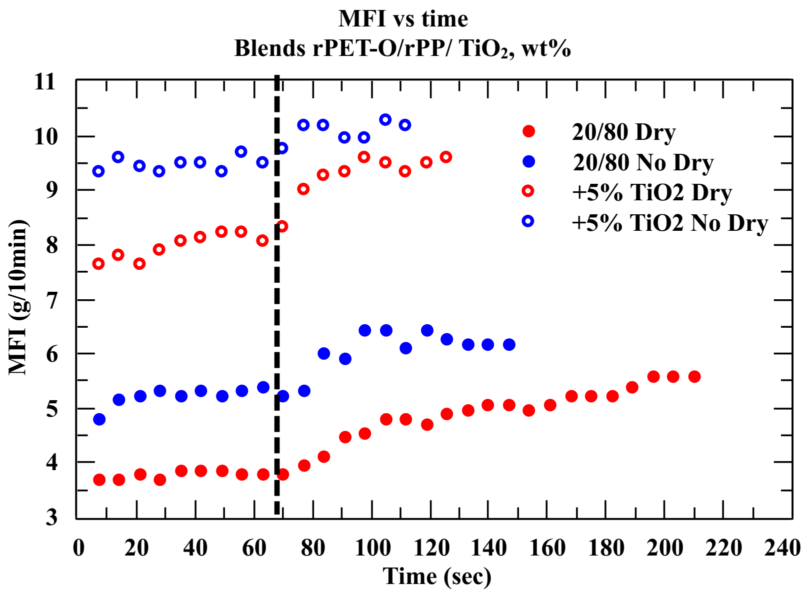
# Phase 2: Blends preparation: rPET-O/rPP: 20/80 + 5%w/w $TiO_2$



# Phase 2: Blends preparation: rPET-O/rPP: 20/80 + 5%w/w $TiO_2$

### *Melt Flow Index (MFI)*

**Methodolgy:** ISO 1133
**Condition:**230ºC/ 2,16 kg (PP as reference)




| Samples | MFI (dg.min$^{-1}$) |
|---|---|
| *Ref. rPP* | 17,7±0,7 |
| 20/80 Dry | 3,8±0,1 |
| 20/80 No Dry | 5,6±*0,3* |
| 20/80 + 5%TiO2 Dry | 8,0±*0,2* |
| 20/80 + 5%TiO2 No Dry | 9,4±*0,3* |

- $TiO_2$ confers greater fluidity
- At 230ºC a residence time < 70s is recommended

### *$TiO_2$ content determination*

**Methodolgy:** ISO 3451-1 (Method A)
**Drying condition:** 120ºC/ 1h15min /vacuum oven
**Calcination temperature:** 1200ºC (oven)/ 3h
**Nº of samples**: 5
**Weigth of sample:** 10 g.

**8,3 % (± 0,5) w/w**

# Phase 3: Blends quality assesment

**Collin® twin screw extruder**
(7 heating zones, L/D =36, D: 25 mm)

**+ 3 vertical roll calendering**
**($\phi$ = 70 mm)**
**Collin® Teachline CR72T**

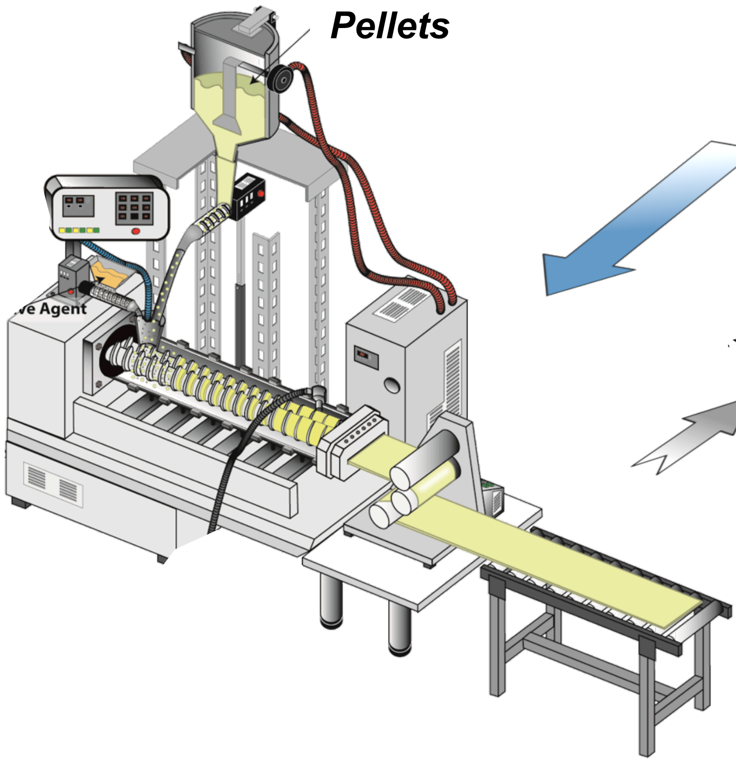
Dried **blends pellets**
(dw: -40ºC, 100ºC/4h)

***TEMPERATURE PROFILE***
*140/180/195/205/215/215/210 (Die)*
*Screw rotation speed: 55 rpm*

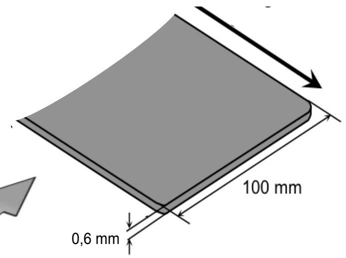
**calendering**
*(20 m)*

Chilling rolls: 50ºC / 2,4 to 2,6 RPM

***Pellets***




***Extrusion flow direction (MD)***




***Morphology inspection***
(SEM observations)

***Tensile tests***

***Falling weight impact tests***

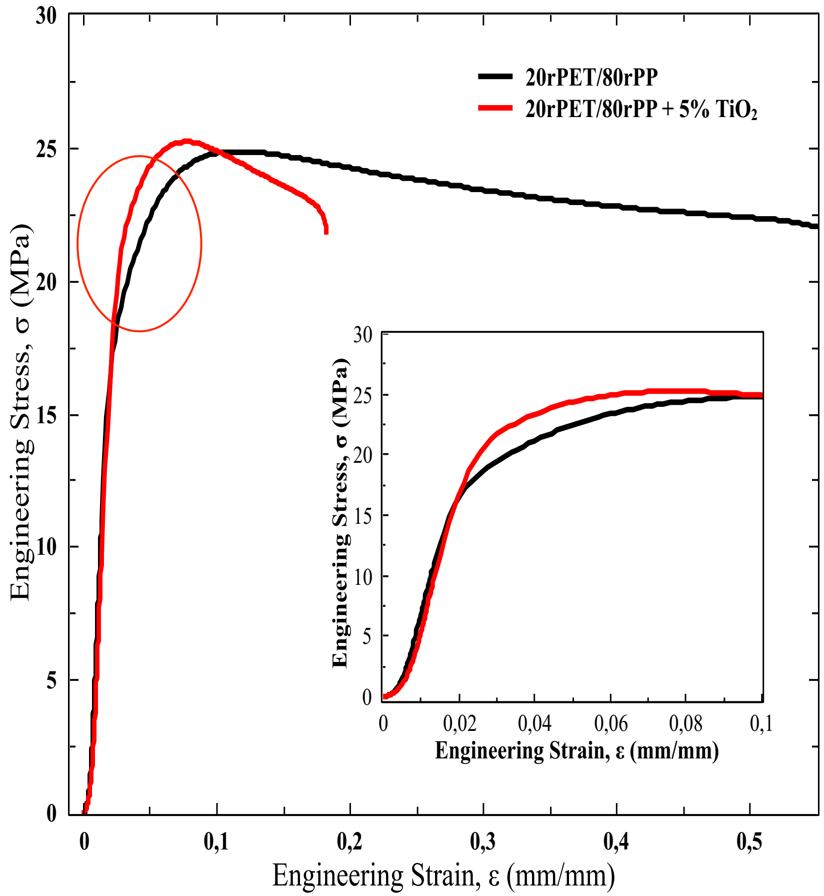
**Fracture (tearing) behaviour *(EWF)***

***HDT/DMTA***

# Phase 3: Blends quality assesment

***Tensile tests:***

**Methodology:** ISO 527 – samples type 4 (flow direction)
**Equipment:** Universal testing machine GALDABINI 2500 + Videoextensometer MITRON OS-65D
**Velocity:** 20 mm.min$^{-1}$
**Temperature:** 18ºC ± 2ºC

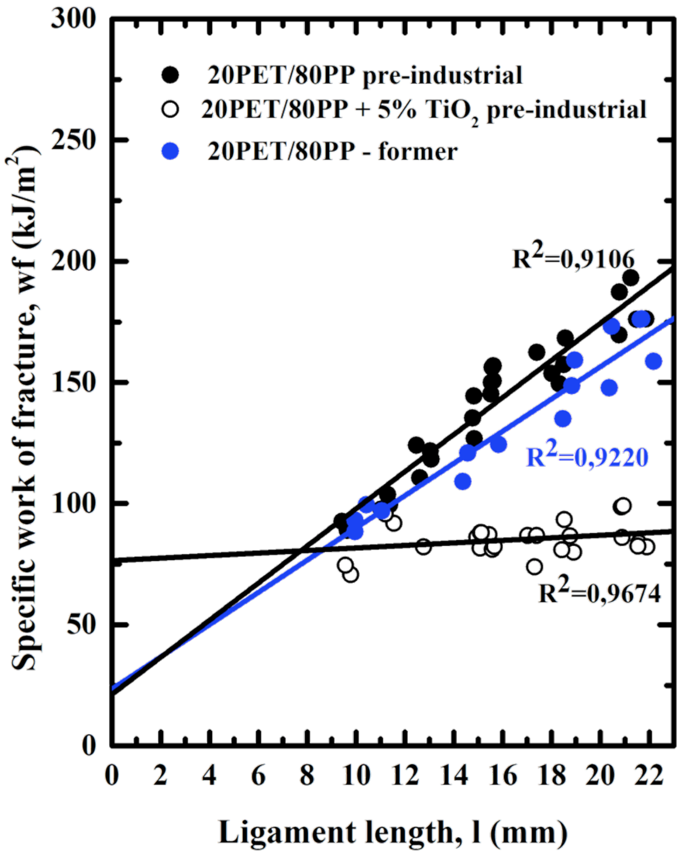



| Sample | Elastic Modulus E [GPa] | Yielding Stress σy [MPa] | Yielding Strain εy [%] | Strain at baeak εb [%] |
|---|---|---|---|---|
| 20rPET-O/80rPP | 1,22 ± 0,02 | 24,9 ± 0,2 | 10,94 ± 0,03 | 34 ± 10 29% |
| 20/80 + 5% TiO2 | 1,24 ± 0,07 | 25,1 ± 0,3 | 7,7 ± 0,2 | 24 ± 13 |
| 20PET/80PP | 1,16 ± 0,07 | 24,0 ± 0,7 | 11,1 ± 0,7 | 77 ± 34 50% |

# Phase 1: “Raw” rPET-O homogenization

***Tearing behavior (Slow crack propagation): Specific work of fracture:***

**Methodology: ESIS-TC4**
**Equipment:** Universal testing machine GALDABINI + viedoextensometer MITRON OS 65D
**Velocity:** 10 mm.min$^{-1}$
**Temperature:** 18ºC ± 2ºC
**Sample geometry:** DDENT
**Nº of tested samples**: 15




| Material | $w_e$ $(KJ.m^{-2})$ | $\beta w_p$ $(MJ.m^{-3})$ |
|---|---|---|
| 20rPET / 80rPP-New | 21,3 ± 7,5 | 7,6 ± 0,4 |
| 20rPET / 80rPP + 5% TiO2 New | 78,9 ± 8,0 | 0,4 ± 0,1 |
| *20PrET / 80rPP Former* | *23,5 ± 8,8* | *6,6 ± 0,5* |

*Thank you*


# Centre Català del Plàstic-UPC

Campus Diagonal-Besos
Edifici C
Av. Eduard Maristany,14-16
Barcelona

Tel. 937.837.022

http://www.upc.edu/ccp

orlando.santana@upc.edu

maria.lluisa.maspoch@upc.edu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# Action 5

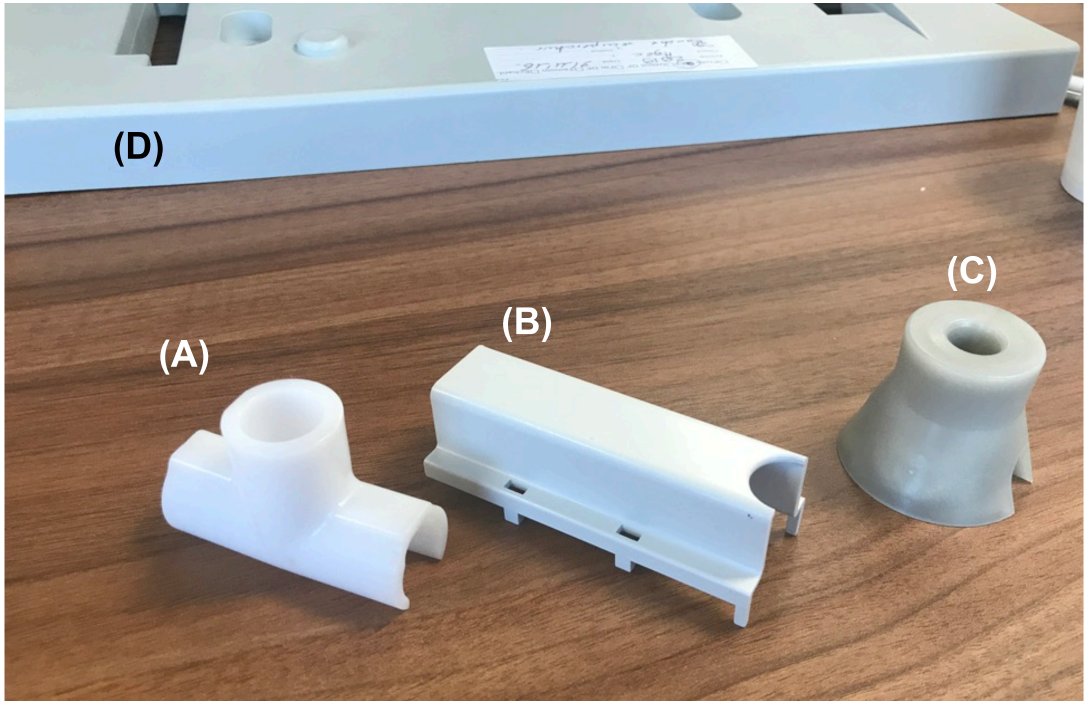
# Prototypes preparation and pre-indsutrial validation

Magali KLOTZ
Hired Technisian formaly contracted from November 15.
Ing. Msc. Material Science and Engineering form EEIGM – UPC.

**Mª Lluïsa MASPOCH RULDUÀ**
CCP-UPC Director.

**Orlando SANTANA PÉREZ**
CCP-UPC Characterization and fracture coordinator.

# Parts considered (after visit to Odoul).




***All parts are manufactured by ODOUL***

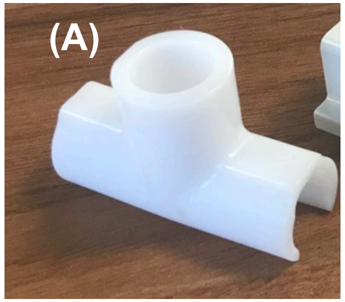
***(A) Hose support used in transfer-infusion moulding***

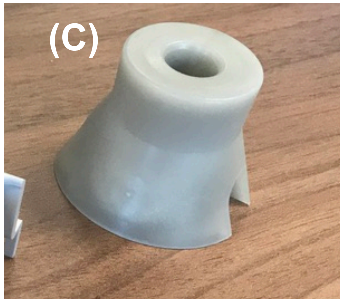
***(B) Profile for mounting electrical panels***

***(C) Hose support used in transfer-infusion moulding***

***(D) Container base for recycling batteries.***

# Requirements

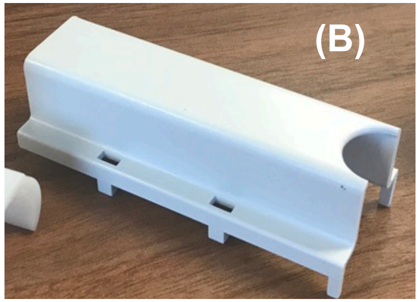



***(A) And (C) Container base for recycling batteries:***

- ✓ Usually made of PP (¿?)
- ✓ **(A)** Optimized geometry – **(B)** Over-dimensioned (so thick)
- ✓ Mechanical requirements: None
- ✓ Some chemical resistance (to solvents)
- ✓ Something of weight to serve as a support
- ✓ **(A)** Two “submarine” injection points (at least) in the inner part.
- ✓ For the "pre-industrialization" test, 10 kg (for each geometry) of material are required
- ✓ ***It is proposed to test with rPET-O and selected mixture.***

# Requirements




***(D) Profile for mounting electrical panels***

- ✓ Usually made of PA66
- ✓ Mechanical requirements: None, just to be flexible enough to make a “clip” action during mounting
- ✓ Electrical (leakage currents resistance) and Fire resistance (V0) (Problems with rPET and PP, requires to be formulated GF + Flame retardant agent)
- ✓ Two “submarine” injection points (at least) in the inner part.
- ✓ For the "pre-industrialization" test, 10 kg (for each geometry) of material are required

***Selected (caution: V0)***

# Proccesing and sample preparation

**Collin® twin screw extruder**
(7 heating zones, L/D =36, D: 25 mm)

**+ 3 vertical roll calendering**
**($\phi$ = 70 mm)**
**Collin® Teachline CR72T**

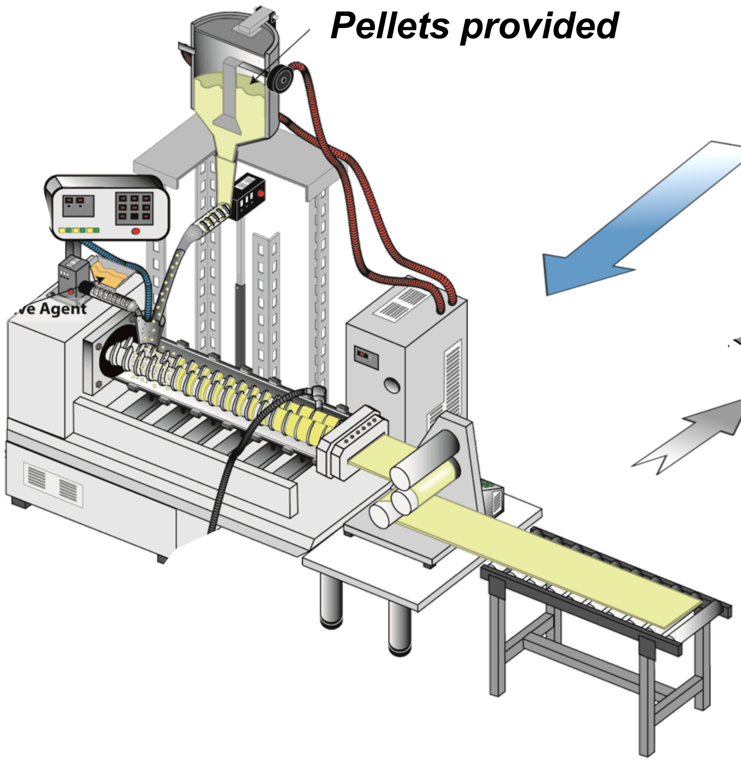
Dried **flakes**
(dw: -40ºC, 120ºC/4h)

***TEMPERATURE PROFILE***
*140/180/195/205/215/215/210 (Die)*

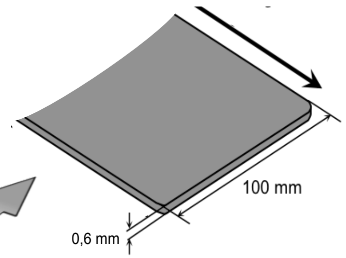
**calendering**
*(5 to 10 m)*

Chilling rolls: 50ºC / 2,4 to 2,6 RPM

***Pellets provided***



***Extrusion flow direction (MD)***

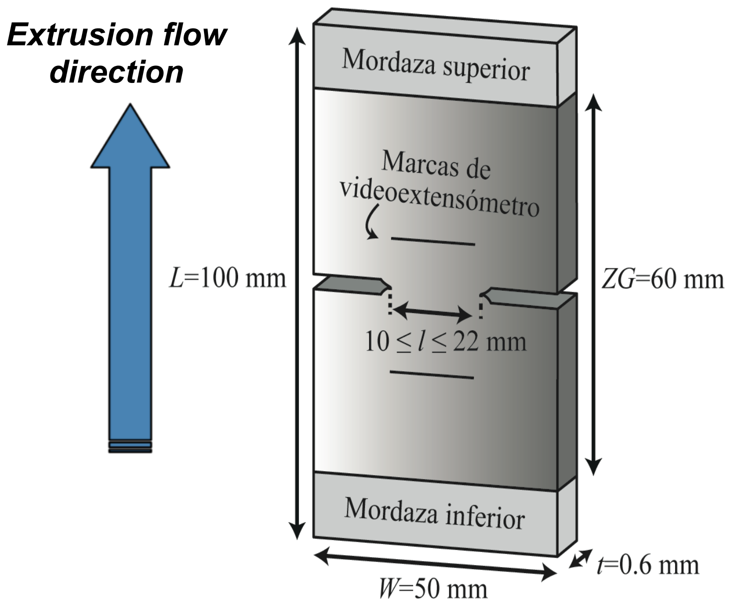



- ***Tensile tests*** @ 25ºC (MD direction)
- ***Morphology inspection*** (SEM observations)
- **Fracture (tearing) behaviour *(EWF)*** @ 25ºC

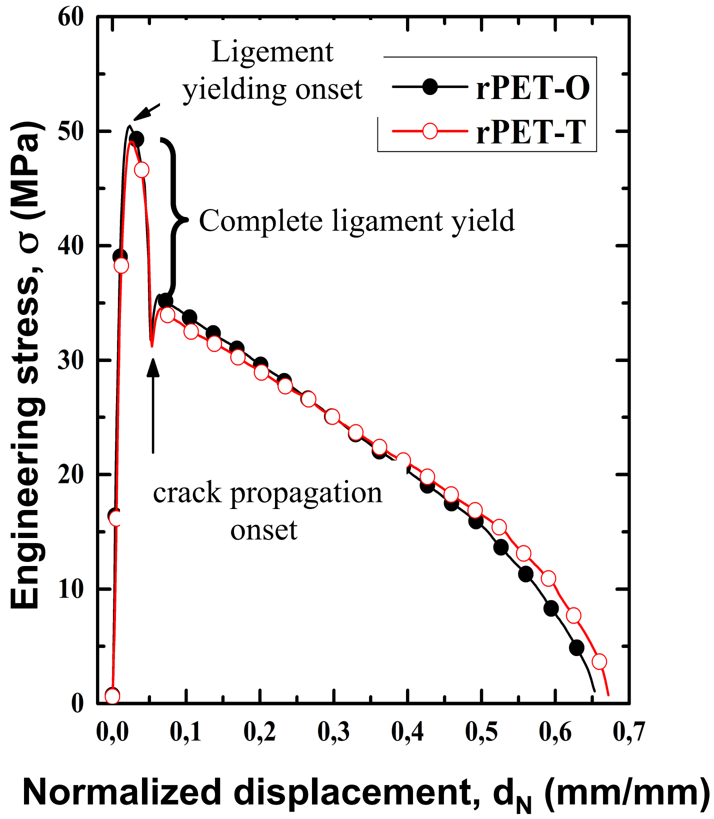
# Phase 1: "Raw" rPET-O homogenization

***Tearing behavior (Slow crack propagation): Specific work of fracture:***

**Methodology: ESIS-TC4**
**Equipment:** Universal testing machine GALDABINI + viedoextensometer MITRON OS 65D
**Velocity:** 10 mm.min$^{-1}$
**Temperature:** 18ºC ± 2ºC
**Sample geometry:** DDENT
**Nº of tested samples**: 15 (3 replicates at 5 ligament length, *l*)




***DDENT geometry used.***
***Crack propagation transverse to flow direction***




***Tipical tests traces. l = 16 mm***