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Caratterizzazione e modellazione di materiali riciclati per la simulazione di processo

RadiciGroup High Performance Polymers
Riccardo Galeazzi

20/06/2024

Moldex3D

RADICI GROUP

Agenda

- Company overview
- Recycled materials in Radici HPP: **RENY**CLE® brand
- Application examples in recycled materials where the process simulation is usefull
- Material card’s properties vs recycled content
- Modelling approach
- Conclusions and further developments

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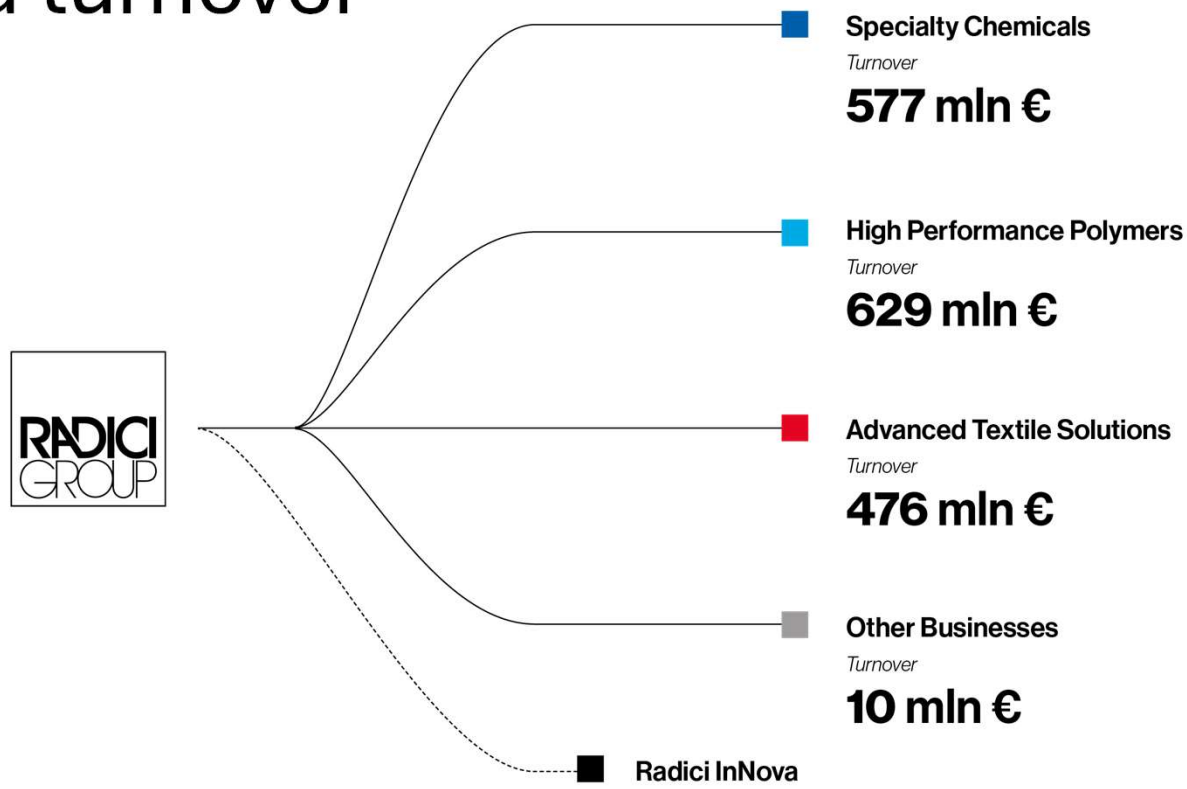
Business area turnover



2022 turnover, consolidated at Business Area level. The figure related to the single Business Area includes sales made to other Business Areas within RadiciGroup.

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High Performance Polymers – Global presence

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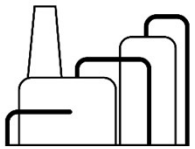
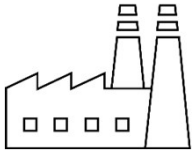
Product definition by raw material sources



Virgin
This material is produced starting from the chemical precursors of the base polymers.



Post-industrial
Material diverted from the waste stream during a manufacturing process.

Post-consumer
Material generated by households or by commercial, industrial and institutional facilities as end-users of products which can no longer be used for their intended purpose.

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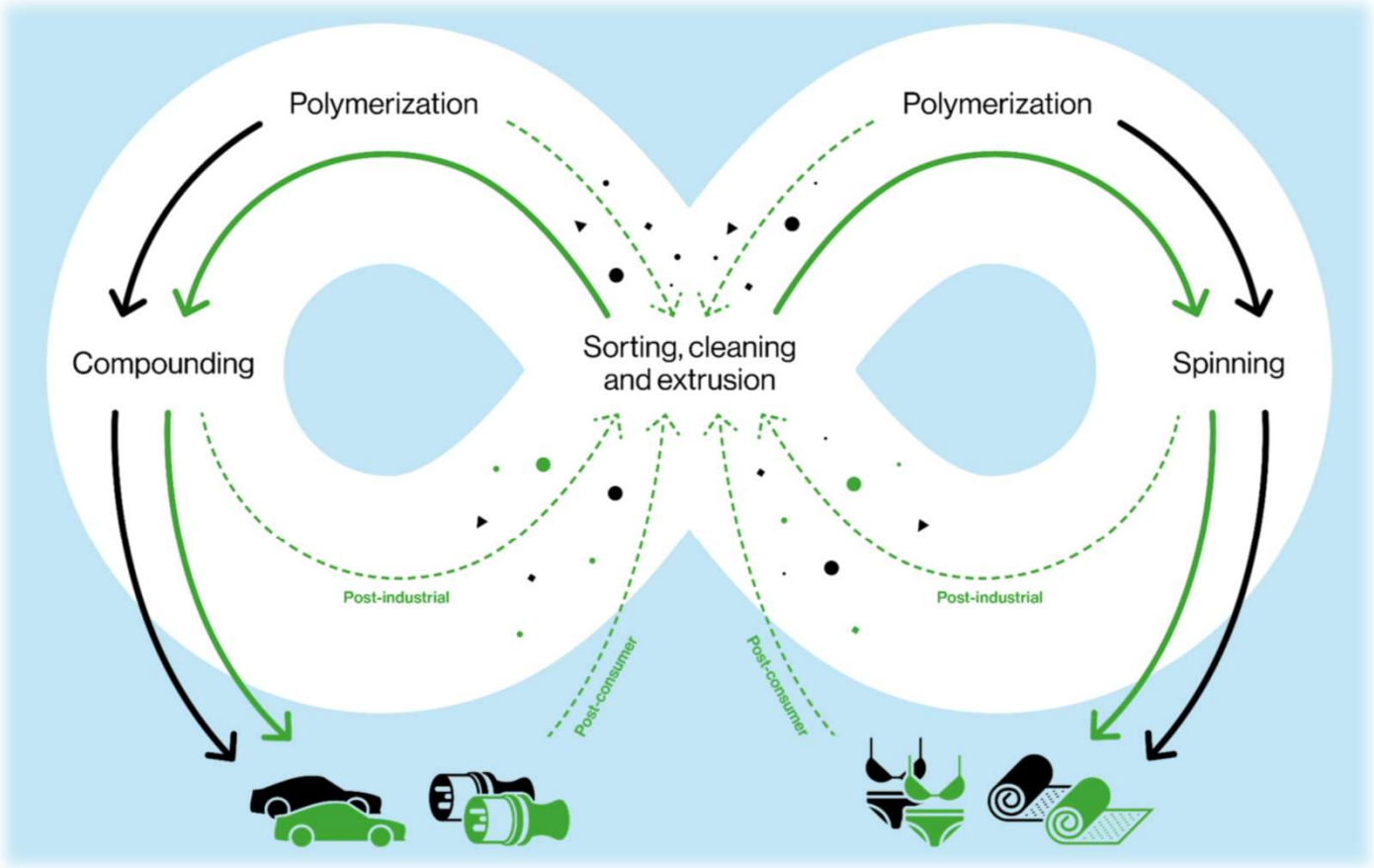
RadiciGroup – Nylon recycling system for circularity

RENYCLE®

nylon after nylon

RadiciGroup is able to **convey scraps either in the same industry which originated them or in a different one**.

It is possible to obtain low environmental impact polyamides, based on **post-industrial** and **post-consumer** sources characterized by **lower and measurable environmental impact**.



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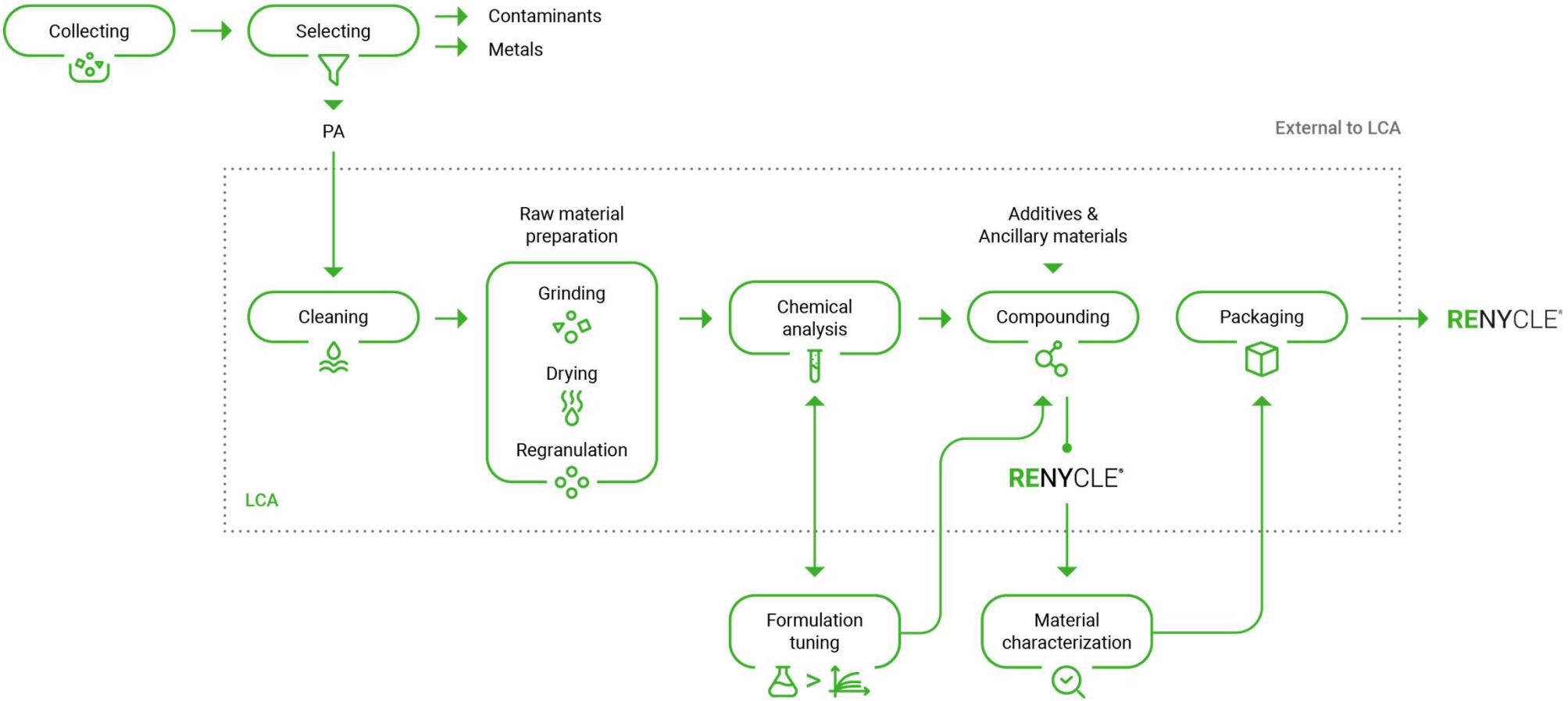
RENYCLE® Production process stages



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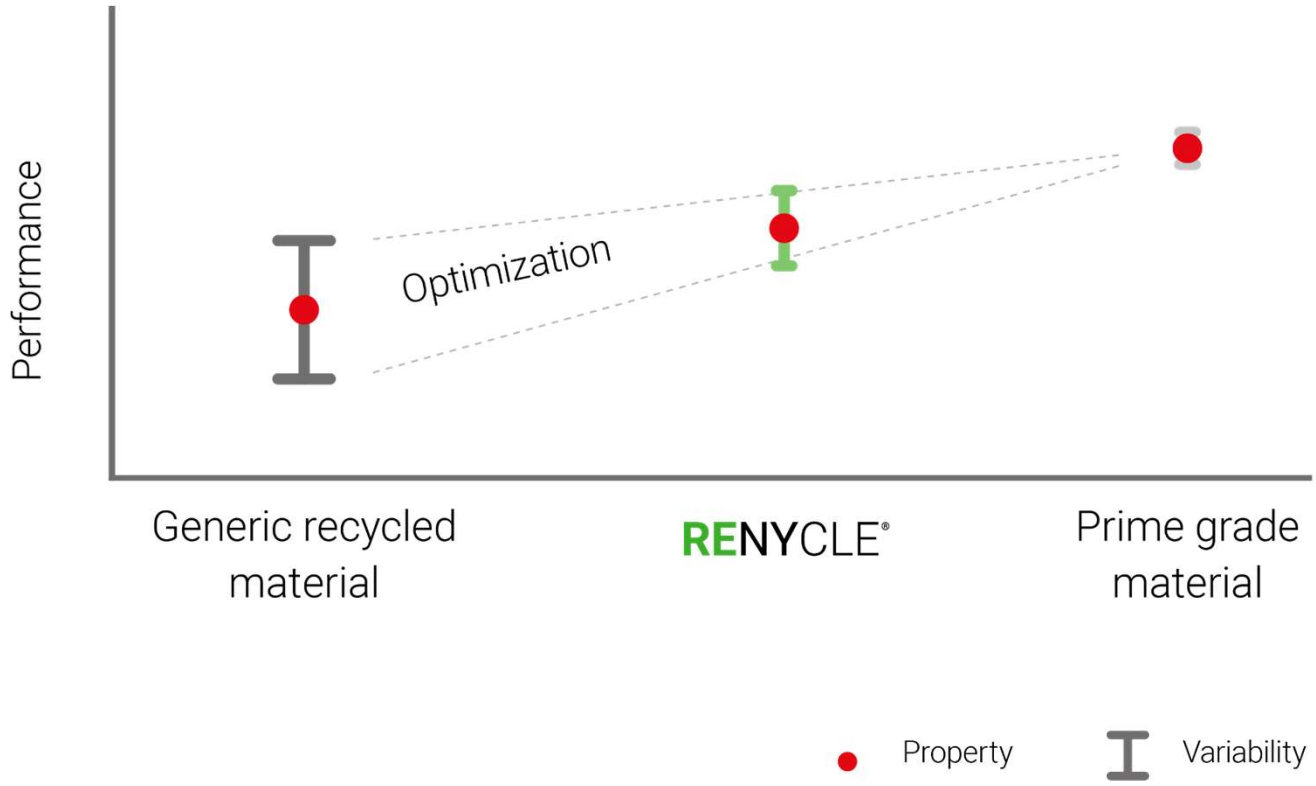
RENYCLE® Goal

The experience gained in post-industrial materials production and the opportunity to participate in circular economy projects has allowed us to develop a production process that **thoroughly monitors raw material selection and treatment** in order to optimize material characteristics and variability.



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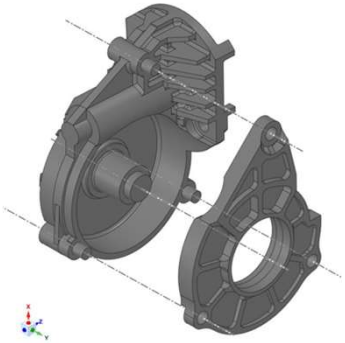
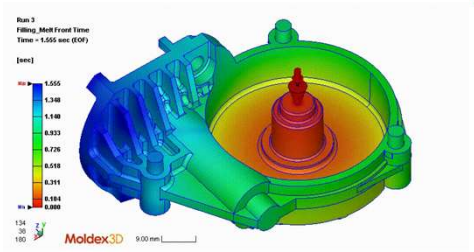
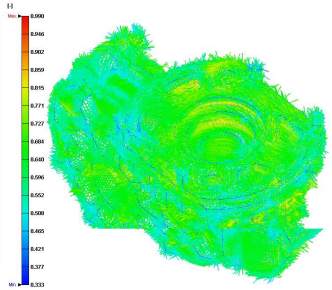
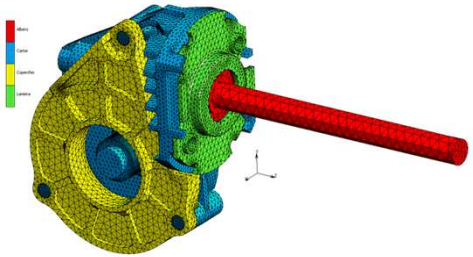
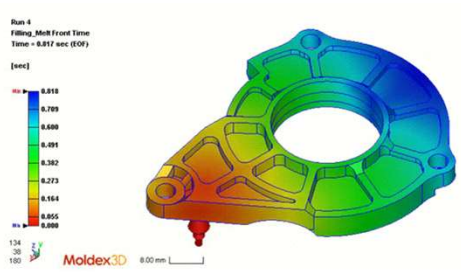
Applications examples in recycled materials where the process simulation is useful (1)

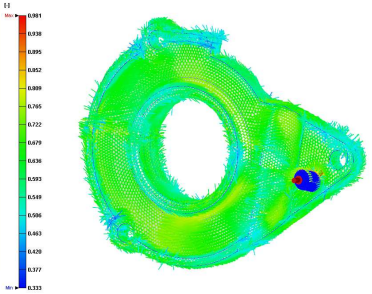


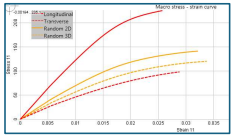


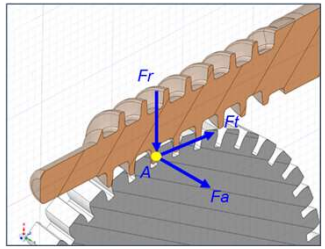


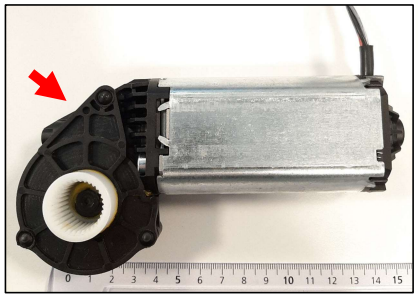








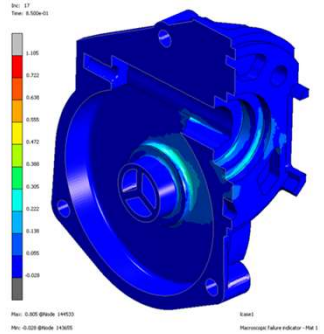




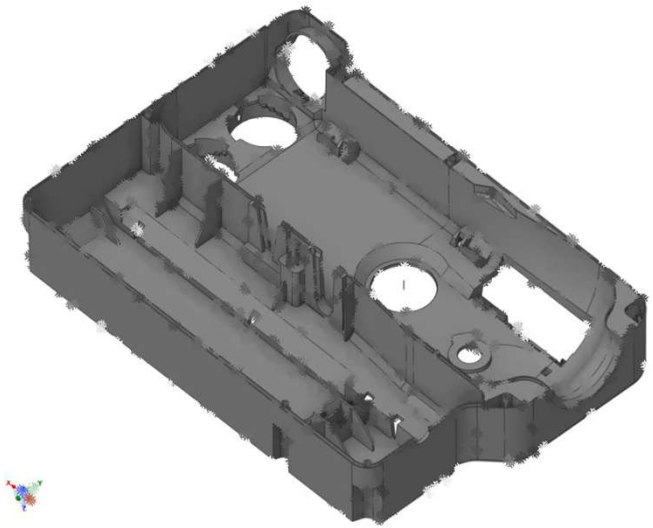
Covers for adjustable desk actuator.
Material used: **Renycle® A GF3004K 3033BK**

The injection molding simulation has been performed in order to hestimate the post-molding warpage, and the fiber orientation distribution for structural simulation.

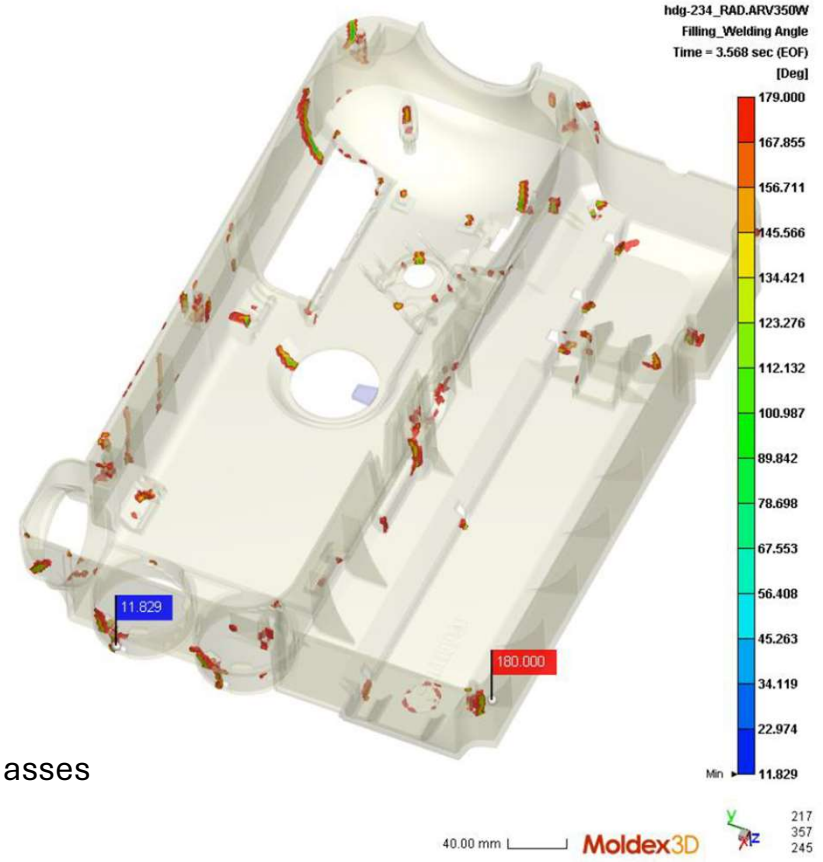
We modelled the stress distribution during usage, comparing the recycled material vs the virgin one.



Applications examples in recycled materials where the process simulation is useful (2)



Housing for industrial application.
Material used: **Renycle® A GF3502K 3033BK**



The injection molding simulation has been performed to asses the weld line severity.

Other applications in recycled materials where the process simulation is useful (3)

Radiator end tanks.
Material used: **Renycle® A GF3002HR 3039BK**

Engine cover.
Material used: **Renycle® S GFK3003K 3033BK**

Fan shroud.
Material used: **Renycle® A GF3004K 3033BK**

Miniature circuit.
Material used: **Renycle® S GF2001 FR2 927F GY**

Injection molding simulation using recycled materials: the scenario (1)

The material cards for the recycled compounds became more and more necessary to incentive the industry to go through *«low environmental impact projects»*.

Considering this, the normal procedure would require to perform the full properties characterization for each recycled material.

But is it really necessary to characterize every time ALL the properties of materials that are very similar to their virgin counterparts, which differ only in their recycled content?

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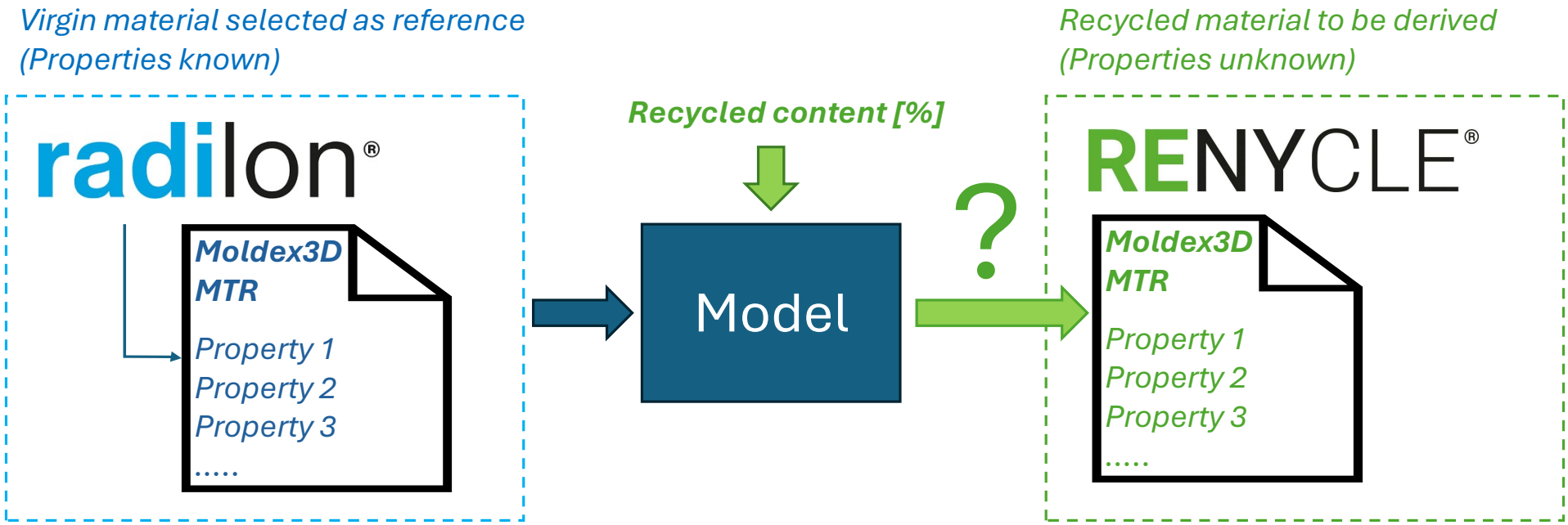
Injection molding simulation using recycled materials: the scenario (2)

Could it be possible to derive in a reliable way the most sensitive properties of the recycled materials knowing those of the homologous virgin material and recycled percentage?



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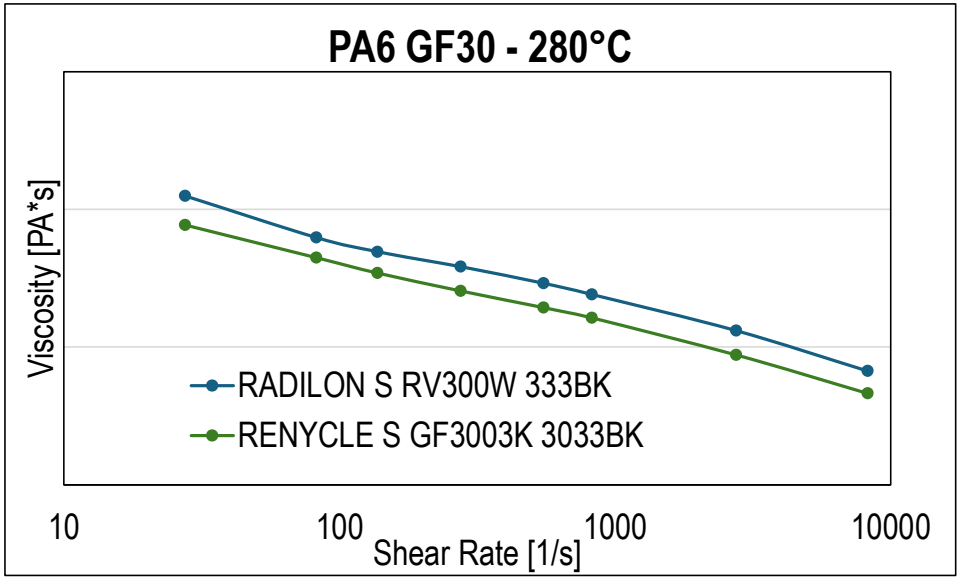
Material card's properties vs recycled content (1)

- Rheological curves

*Necessary for **filling phase** to asses the resistance of material to flow and therefore its pressure and velocities.*



Base material: PA6-GF30

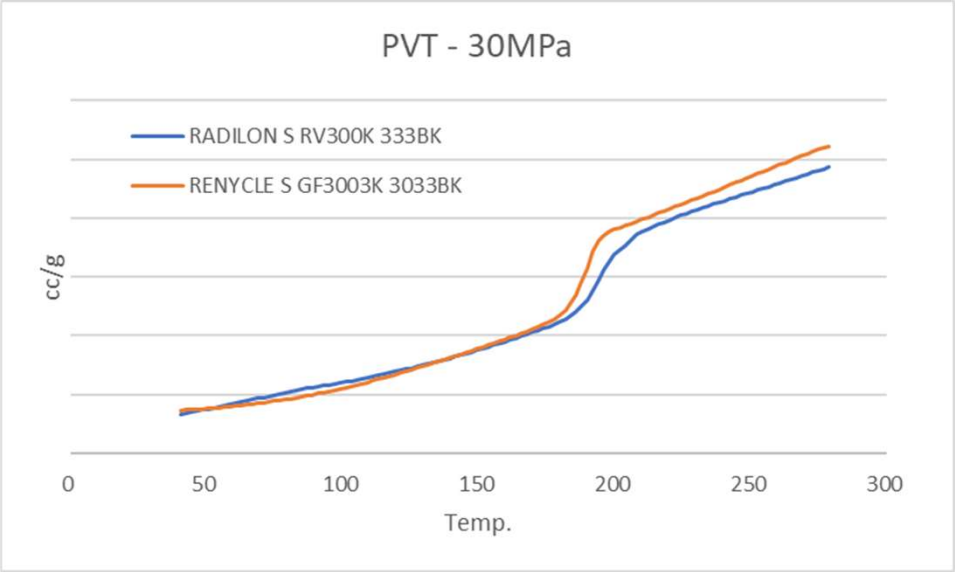
RENYCLE S GF3003K 3033BK – Polymer base fully recycled
RADILON S RV300W 333BK – Virgin material

The viscosity variation between the two grades is significant.

Material card's properties vs recycled content (2)

- Pressure-Volume-Temperature Curves (PVT)

*Necessary for **Packing Phase** to measure volumetric shrinkage of each element and the correspondent pressure while cooling down.*



Base material: PA6-GF30

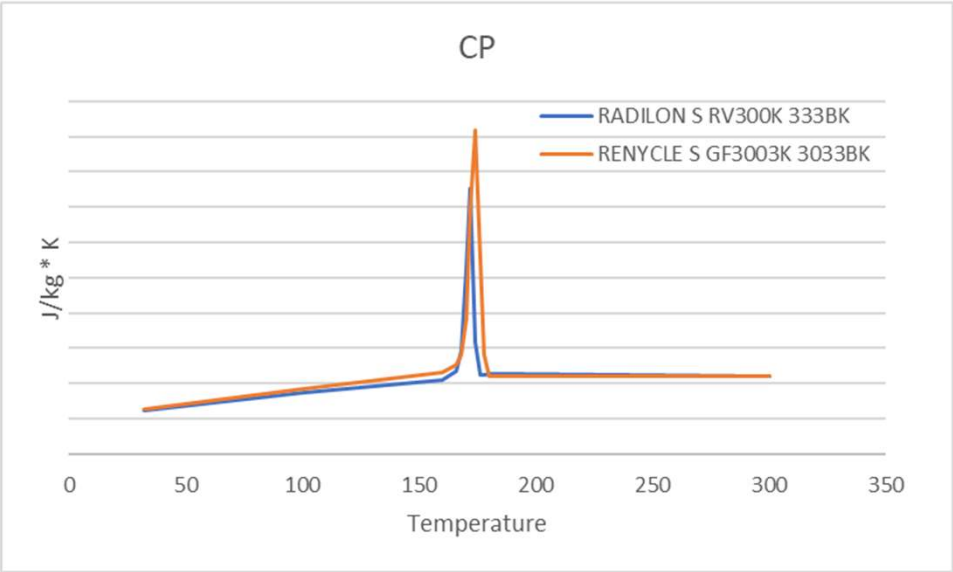
RENYCLE S GF3003K 3033BK – Polymer base fully recycled
RADILON S RV300K 333BK – Virgin material

PVT variation between prime grade and recycled material is lower than 1% especially before 200°C

Material card's properties vs recycled content (3)

- Thermal capacity (CP)

*Necessary for **Filling, Packing and cooling phases** to assess the energy associated with the thermal flow and the solidification point of the material.*



Base material: PA6-GF30

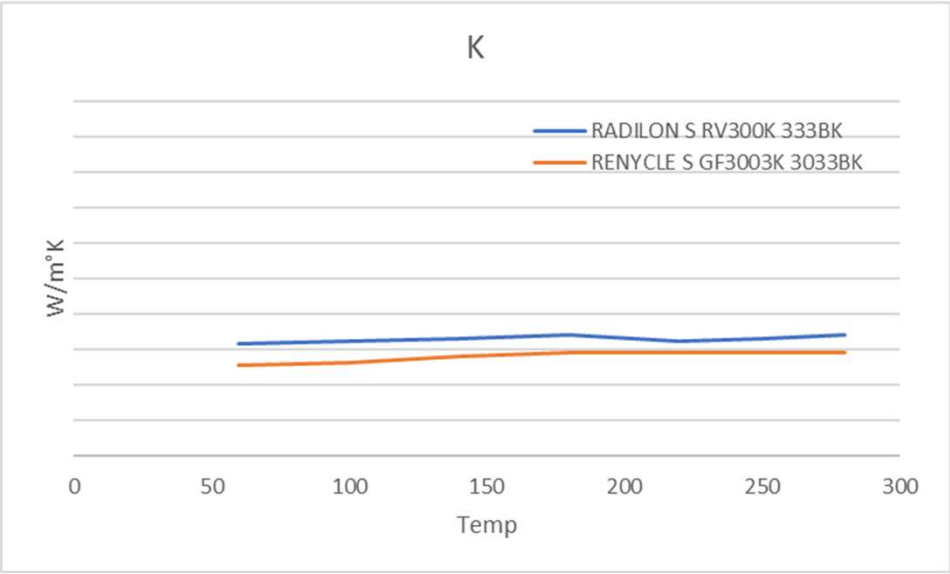
RENYCLE S GF3003K 3033BK – Polymer base fully recycled
RADILON S RV300K 333BK – Virgin material

Transition temperature *RENYCLE → 174°C*
RADILON → 176°C

Material card's properties vs recycled content (4)

- Thermal conductivity (k)

*Necessary for **Filling, Packing and cooling phases** to assess the heat flow rate from element to element and to the mold wall.*



Base material: PA6-GF30

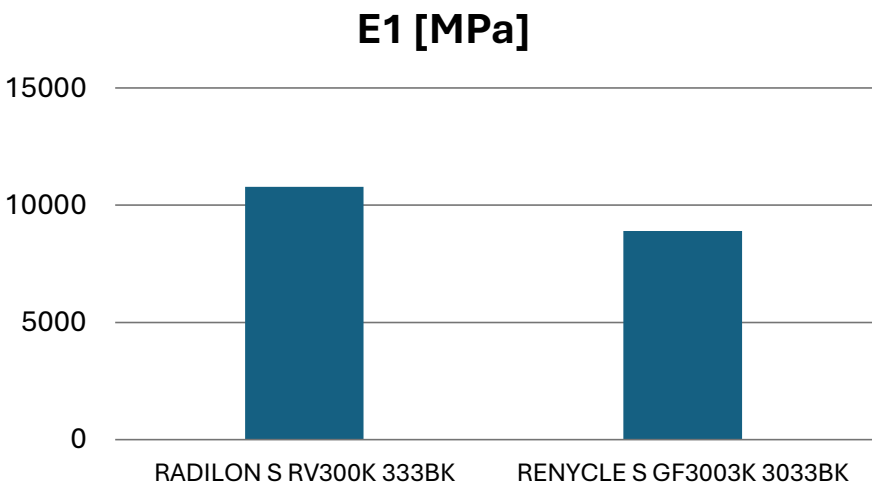
RENYCLE S GF3003K 3033BK – Polymer base fully recycled
RADILON S RV300K 333BK – Virgin material

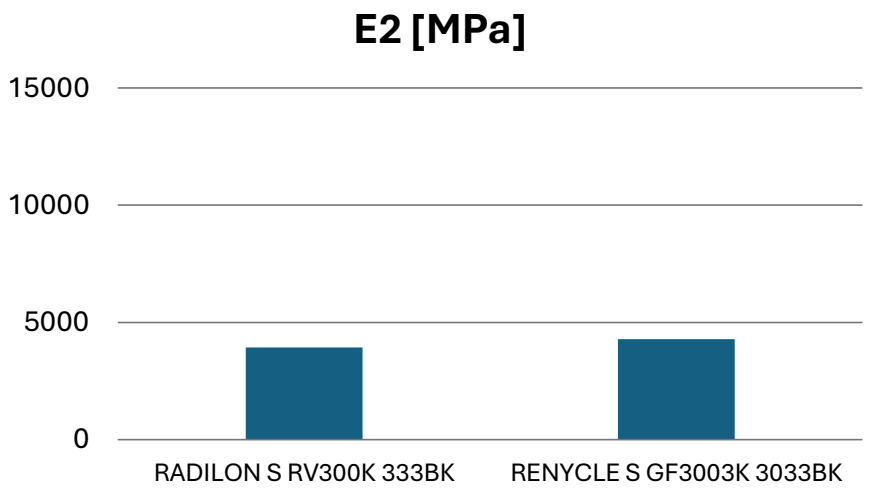
K variation between prime grade and recycled material is not significant.

Material card’s properties vs recycled content (5)

- Mechanical properties (k)

*Necessary for **warpage phase** to calculate stresses and strains associated with the solidification and cooling phases and the anisotropy induced by crystallization and/or filler content.*





Material card's properties vs recycled content (5)

- Considerations
  - Properties like PVT curves, thermal conductivity K, and thermal capacity CP, show a little variation between virgin and recycled materials. Then **for process simulations these properties can be considered equivalent**.
  - **The mechanical properties** like stiffness of the recycled material compared to the virgin one, differs in a quite significant way. But this properties **are simpler to be measured.**
  - **The rheological properties presents not negligible differences between the virgin and recycled materials, especially for the simulation of the filling phase**.

For this reason, we focused our attention the viscosity, trying to modelling it in function of the recycled content:

from 0% - virgin → 100% recycled.

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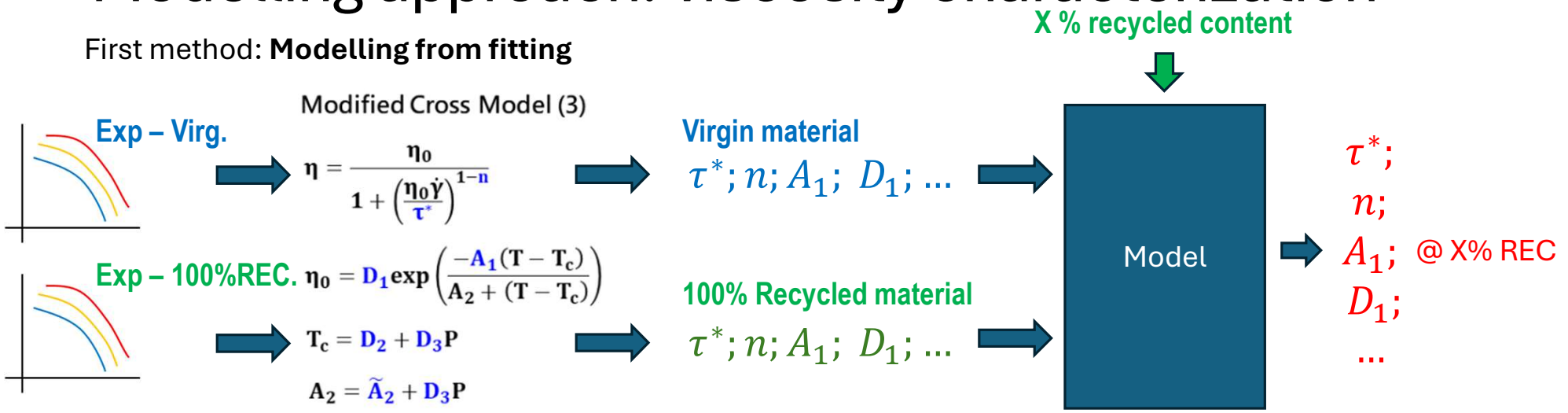
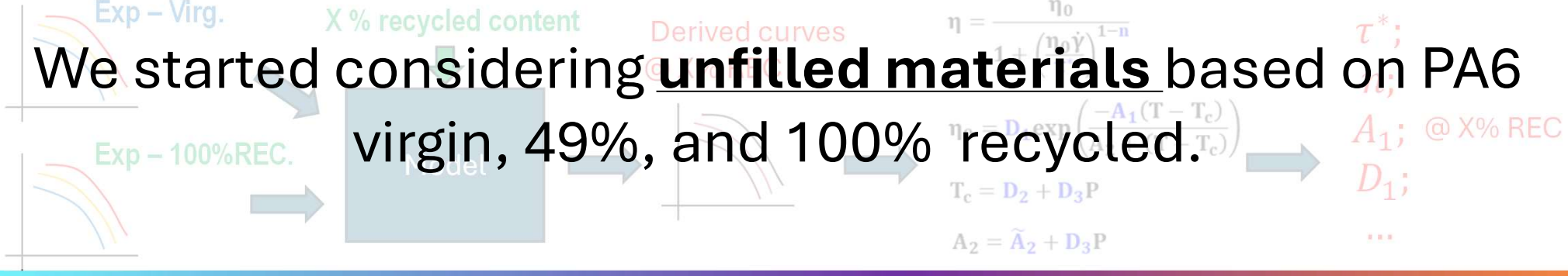
Modelling approach: viscosity characterization

First method: **Modelling from fitting**



Second method: **Modelling from raw data**



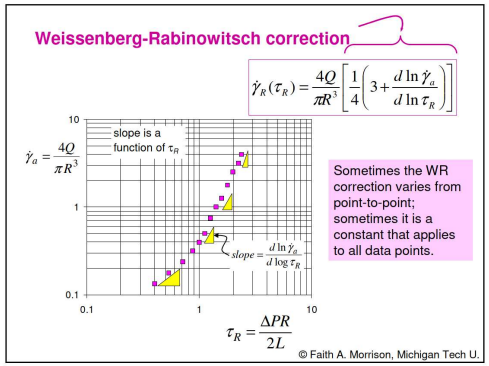
We started considering **unfilled materials** based on PA6 virgin, 49%, and 100% recycled.

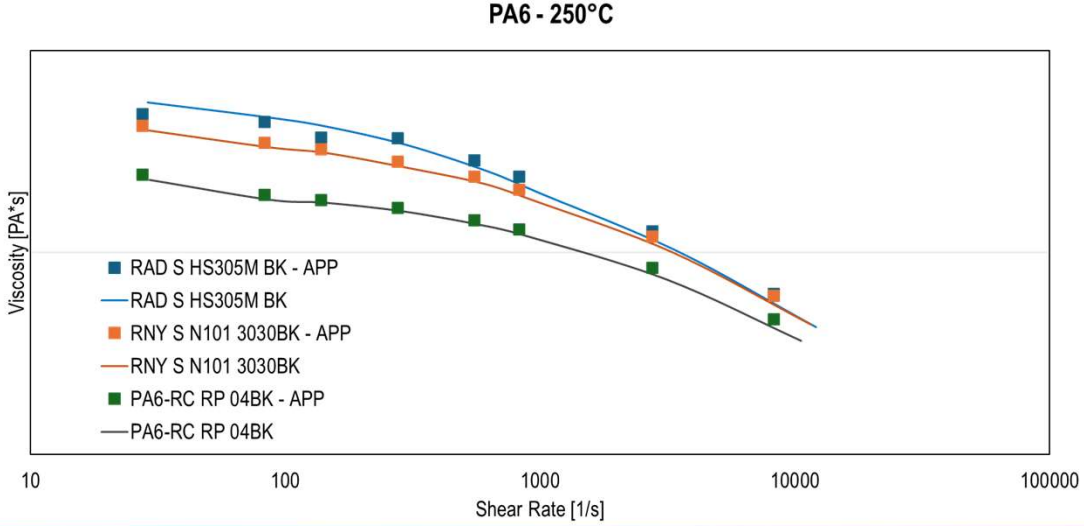
Modelling approach (1): Raw data correction

From the apparent data (shear rate and viscosity), knowing the shear stress, ***we applying the Weissenberg-Rabinowitsch correction in order to compensate the effect of the velocity profile not parabolic in the capillary.***

Forward finite difference between shear rates and shear stresses

$$\dot{\gamma}_w = \dot{\gamma}_{wa}\left[\frac{1}{4}\left(3 + \frac{d\ln(\dot{\gamma}_a)}{d\ln(\tau_r)}\right)\right] = \dot{\gamma}_{wa}\left[\frac{1}{4}\left(3 + \frac{\ln(\dot{\gamma}_{a2}) - \ln(\dot{\gamma}_{a1})}{\ln(\tau_{r2}) - \ln(\tau_{r1})}\right)\right]$$

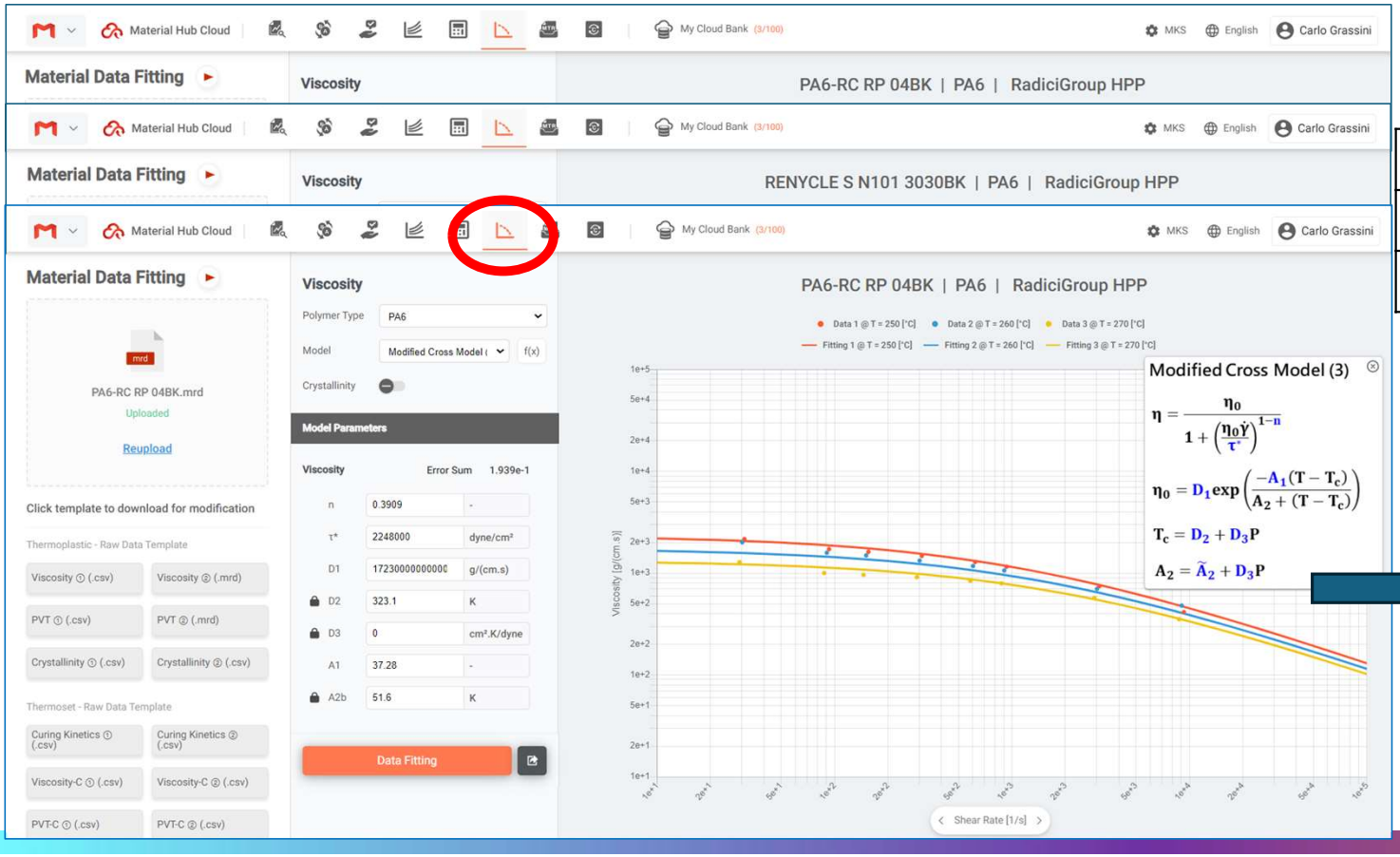




RAD S HS305M BK	**0% REC**
RNY S N101 3030BK	**49% REC**
PA6-RC-RP 04BK	**100% REC**

Modelling approach (2): Moldex 3D M. HUB Fitting

The viscosity data corrected, has been fitted with Modified Cross Model (3) on the Moldex3D Material HUB platform.



RAD S HS305M BK	**0% REC**
RNY S N101 3030BK	**49% REC**
PA6-RC-RP 04BK	**100% REC**

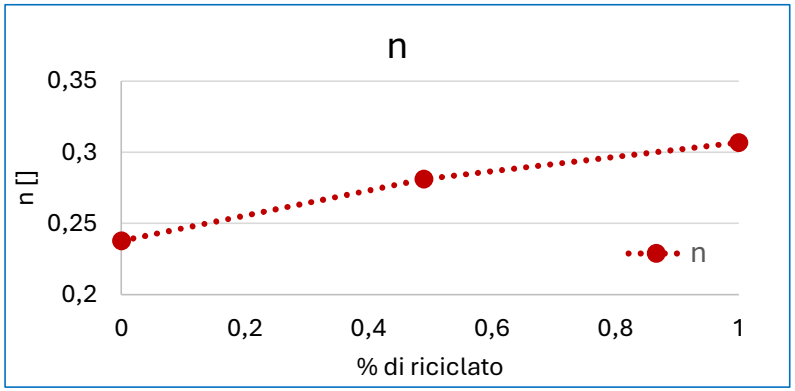
$\tau^{*\#}$;
n;
A_1;
D_1.

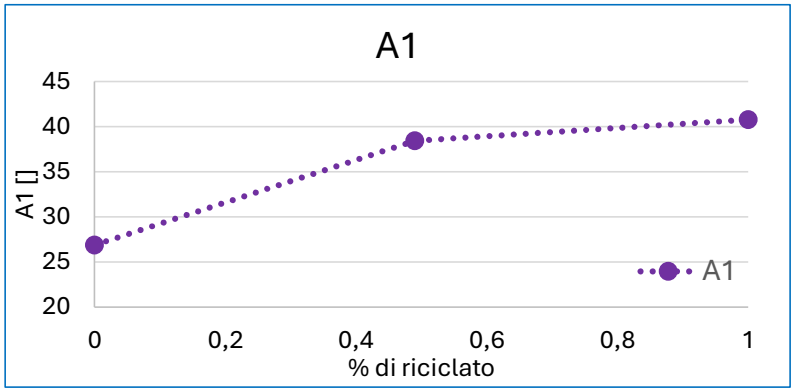
@

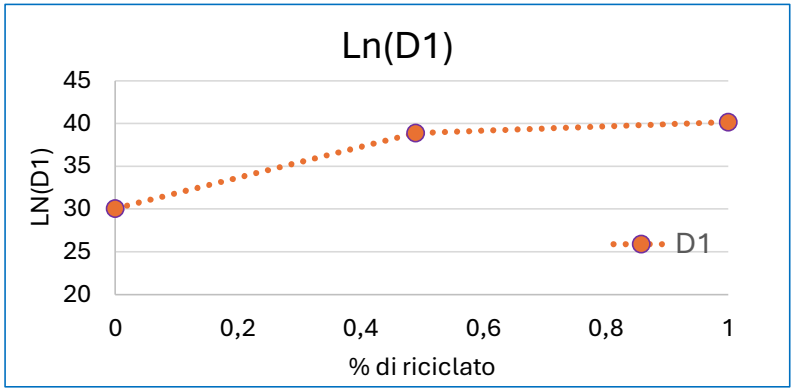
0% REC
49% REC
100% REC

τ^* for the recycled materials, has been imposed equal to the virgin material.

Modelling approach (3): Mod. Cross Model 3 parameters vs %REC





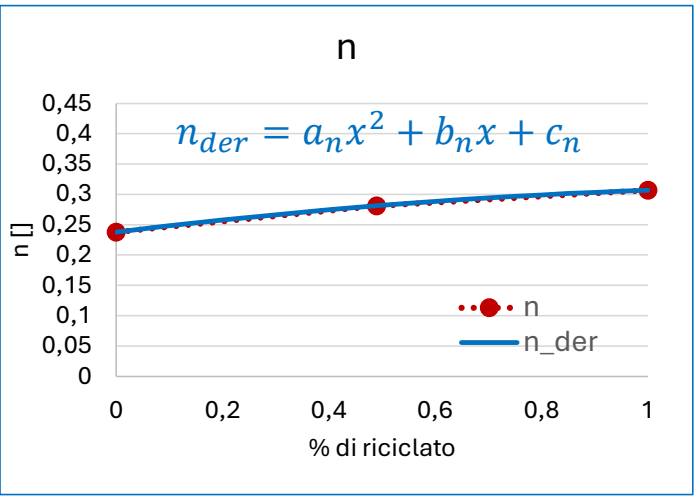


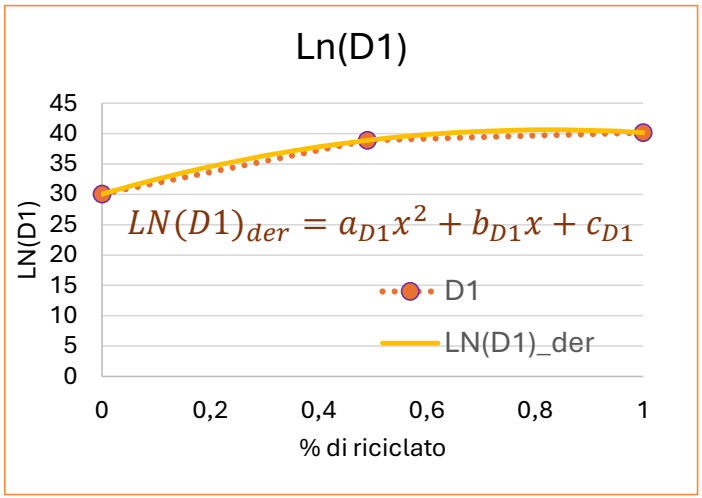
	RAD S HS305M BK	RNY S N101 3030BK	PA6-RC RP 04BK	
n	0.2378	0.2811	0.3069	
D1	1.13E+13	7.725E+16	2.795E+17	g/(cm*s)
A1	26.88	38.4	40.78	
% riciclo	**0**	**0.49**	**1**	

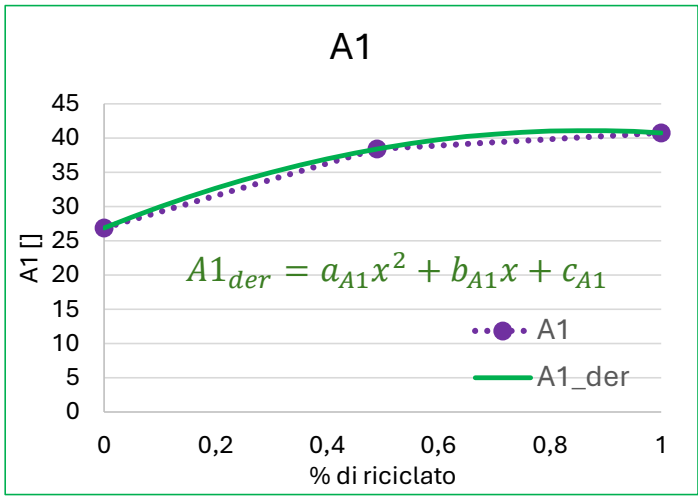
Modelling approach (4): Mod. Cross Model 3 parameters vs %REC

$n;$
$A_1;$ $\longrightarrow$ $y = ax^2 + bx + c$ $\longrightarrow$
$D_1.$ $(\mathrm{x} = \%\ \mathrm{rec})$

$n \rightarrow a_n;\ b_n;\ c_n$
$A_1 \rightarrow a_{A1};\ b_{A1};\ c_{A1}$
$D_1 \rightarrow a_{D1};\ b_{D1};\ c_{D1}$



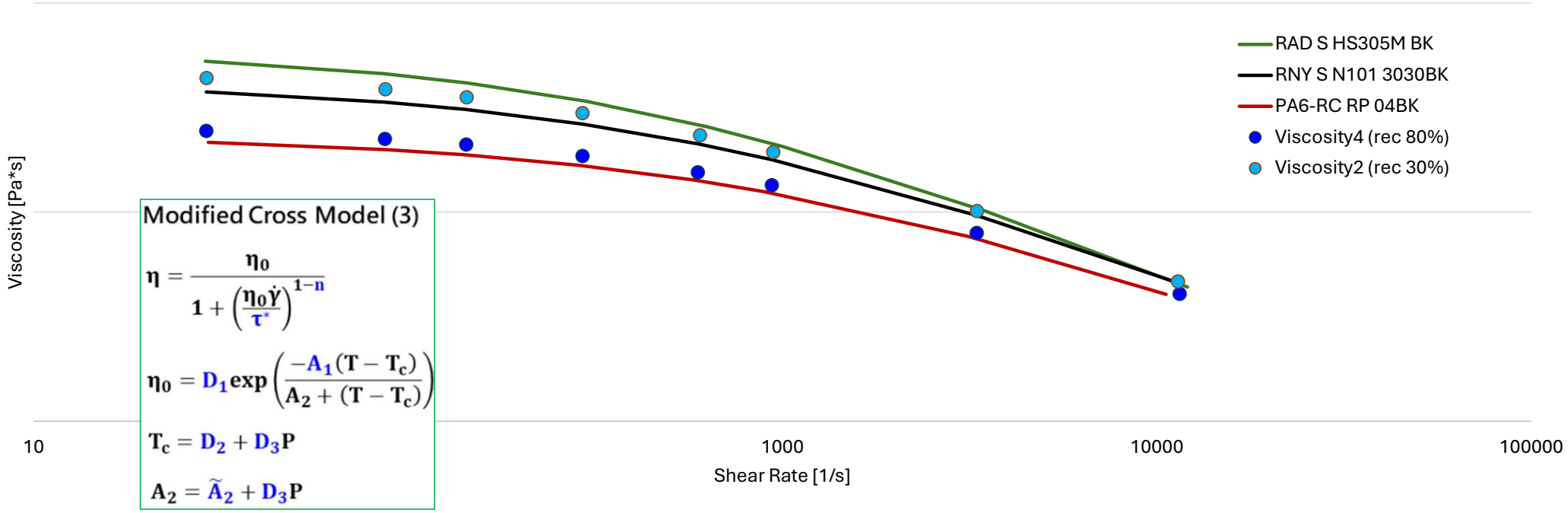




Modelling approach (5): Viscosity estimation vs %REC

***Knowing the % REC** present in the compound, **it is possible to derive** the correspondent Modified Cross Model (3) **parameters (n; A1; D1)**. **Imposing τ* equal to the Virgin material, is now possible hestimate the viscosity** for the recycled material originally unknown.*

PA6 - 250°C



Modified Cross Model (3)

$$\eta = \frac{\eta_0}{1 + \left(\frac{\eta_0 \dot{\gamma}}{\tau^*}\right)^{1-n}}$$

$$\eta_0 = D_1 \exp\left(\frac{-A_1(T - T_c)}{A_2 + (T - T_c)}\right)$$

$$T_c = D_2 + D_3 P$$

$$A_2 = \widetilde{A}_2 + D_3 P$$

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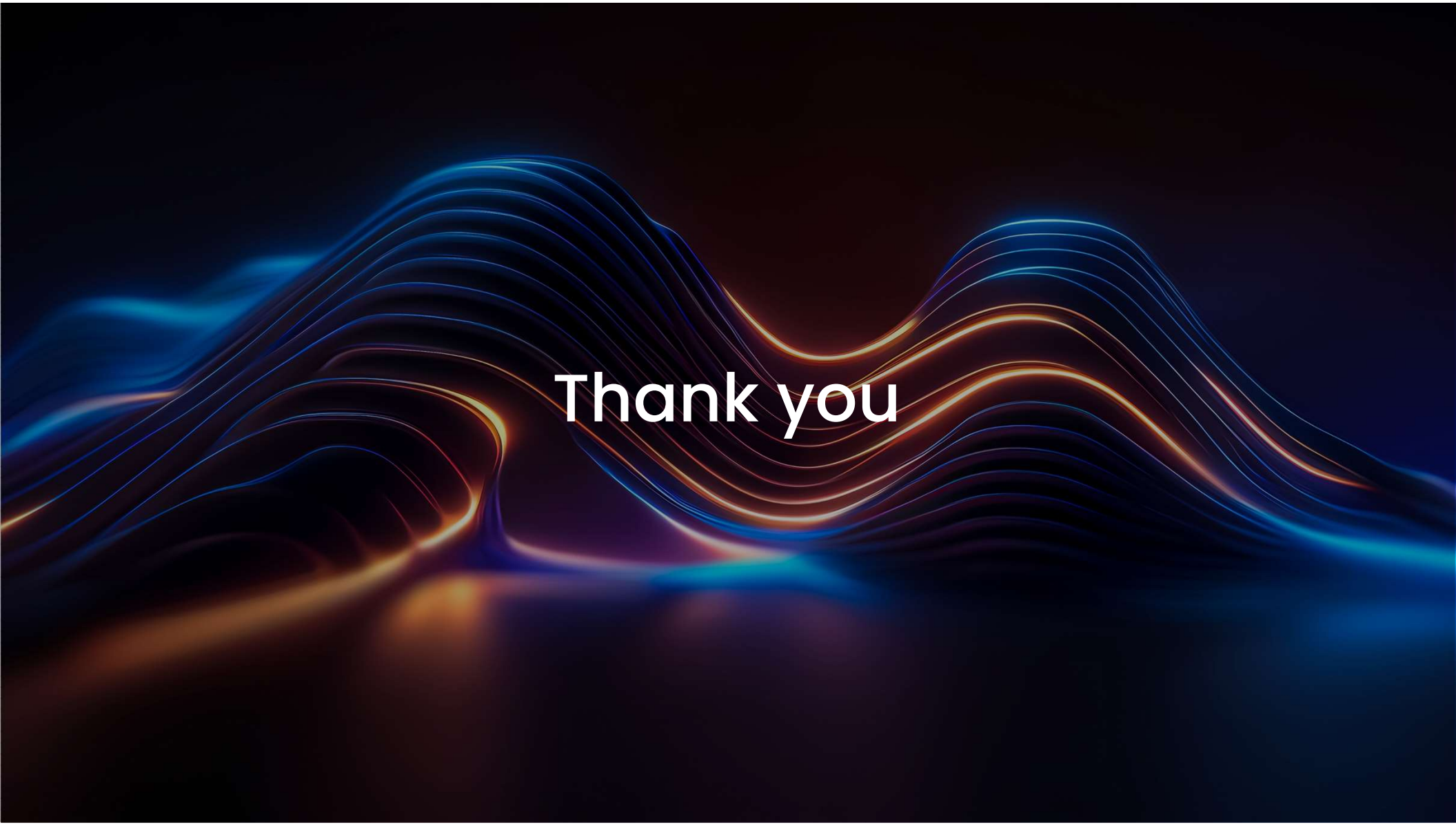
Conclusions & Further developments.

- We applied this approach to an unfilled material. It is necessary to extend it to fiber reinforced materials.
- It is necessary also to validate the approach, considering other virgin materials as reference (impact-modified materials, flame retardant, etc.)
- We focused our attention on modeling the fitted parameters of the viscosity. Interestingly will be also verify the feasibility to treat directly the experimental viscosity curves to derive those of the recycled material and then then applying the fitting.
- Second level validation will be using these results to build Moldex3D material cards and then verify the result of process simulations ran using derived data for recycled materials.


Thank you