Reactive extrusion for the purification of recycled PET for food contact applications.

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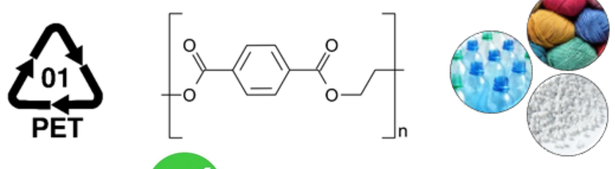
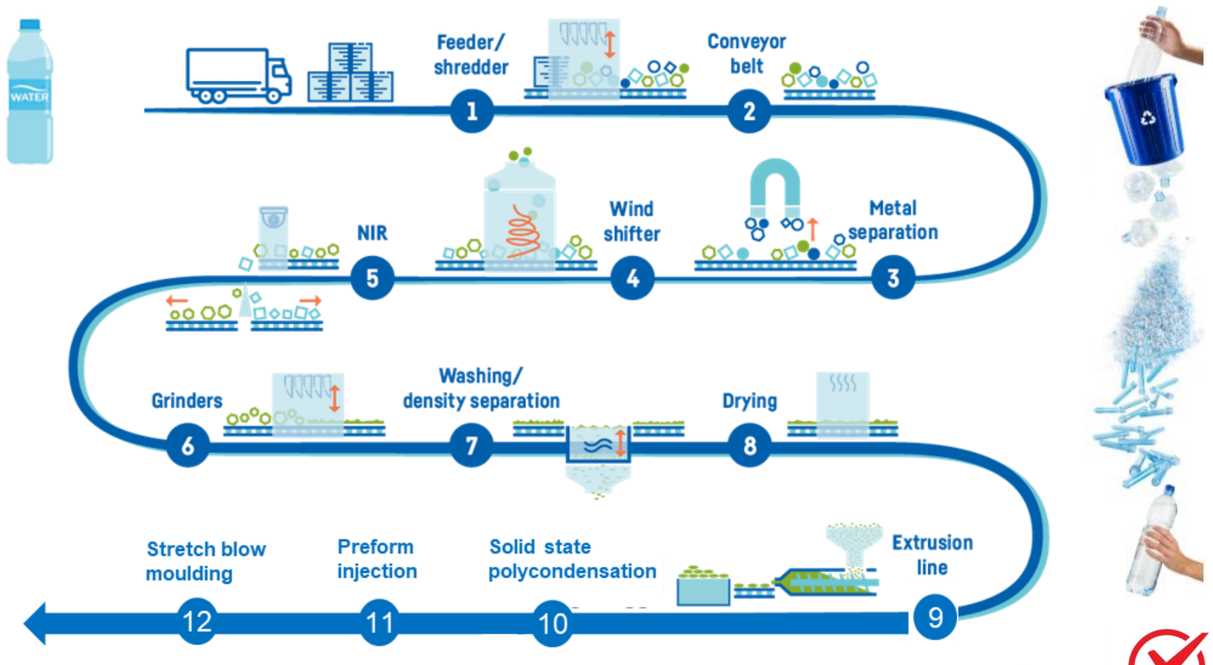
Introduction :



(+) PET mechanical recycling

- Mechanical recycling is backed by strong **life cycle analysis**.
- Polyethylene-terephthalate (PET) is 3rd common polymer in packaging.
- **Food-contact PET** recycling has seen notable **growth** driven by regulation.



(-) Recycled PET (**rPET**) is contaminated with Non-Intentionally Added Substances (NIAS) such as **benzene :**

- NIAS can **migrate** from rPET into water / food ➔ EU regulations define maximum allowed levels to mitigate public health risks.
- NIAS contamination **limits** the use of rPET in food-contact packaging.

Problem to solve :

A recent study proved that benzene content is connected to sorting quality (1).

A secondary material: PVC present due to sorting limitation (same density as PET) degrades at PET processing **temperature** during mechanical recycling and **releases benzene**

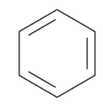


Fig. Benzene

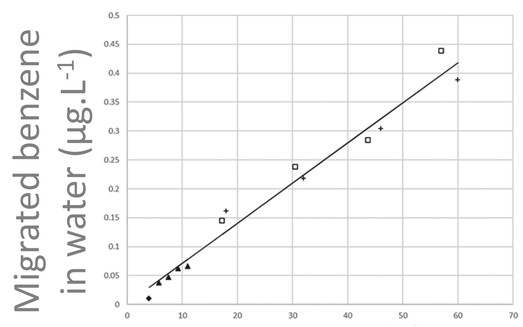


Fig. Benzene content in water VS PVC content in PET

PVC thermal degradation leads predominantly and counterintuitively to benzene through a radical mechanism (2).

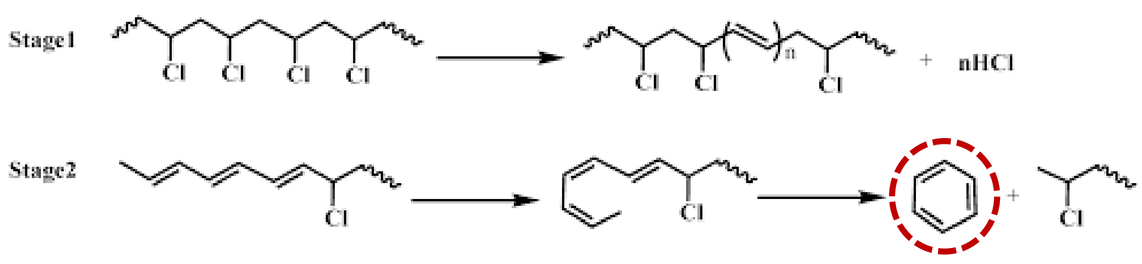


Fig. Degradation of PVC ➔ benzene

(1) *Effect of recycled content and rPET quality on the properties of PET bottles, part II: Migration. Packag. Technol. Sci. 33, 359–371 (2020).*
(2) *PVC thermal degradation. Polym. Degrad. Stab. 49 181 (1995).*

Hypothesis :

- Adding specific **pro-degradants** to the melt can selectively alter NIAS precursors.
- Use of **Reactive Extrusion** (REx) as a fast, continuous and scalable tool to reduce NIAS levels in rPET .

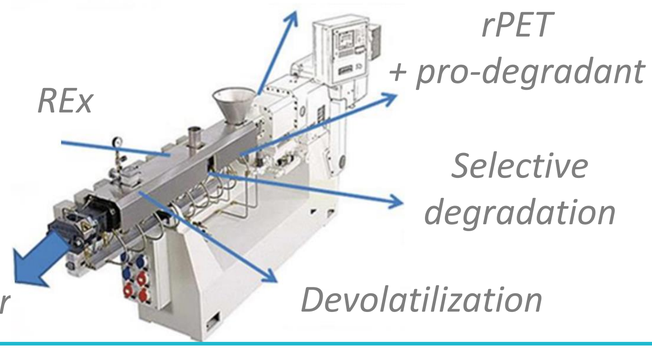


Fig. Twin screw extruder

Objectives :

- **Selective purification / degradation** of benzene, during PET mechanical recycling.
- While **avoiding rPET degradation**.
- Develop a sustainable and cost-effective solution “plugged and plays” for the recycling industry.

New method for PET purification:

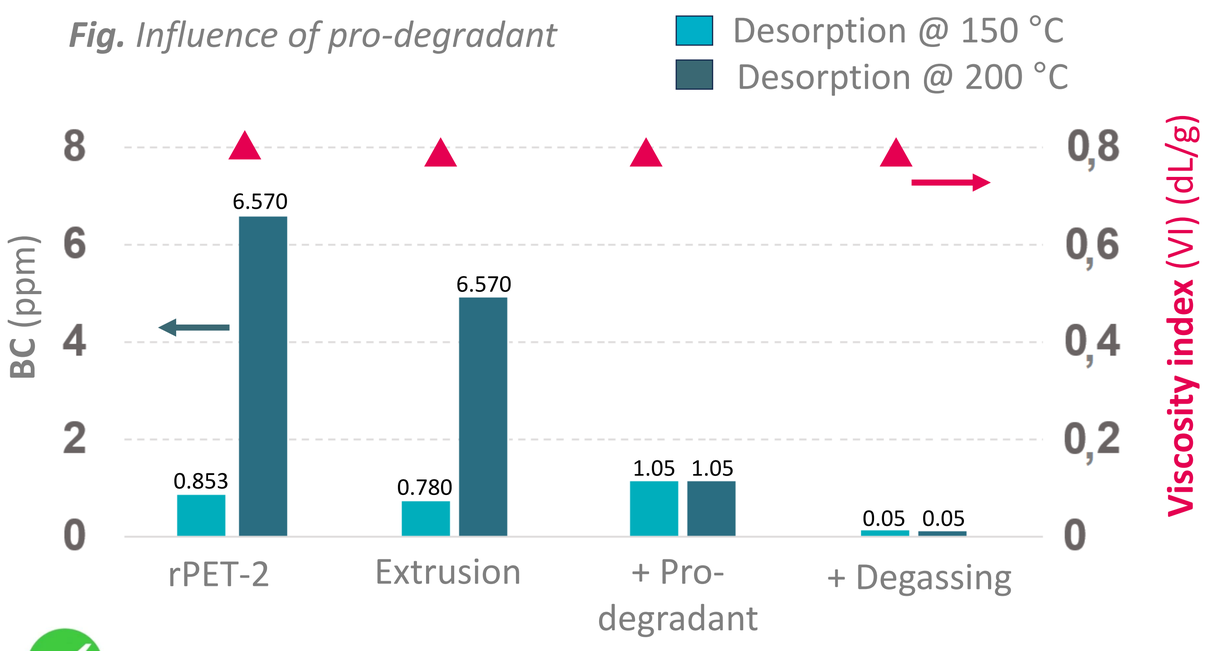
Raw materials :
Neat PET
rPET-1 / low benzene
rPET-2 / high benzene

Various types of **pro-degradants** (s), (l) or (g) were tested with various melting points and activation temperatures

Melt processing conditions :
T : 250 °C
Screw speed : 100 rpm
Residence time: 2 min
Atmosphere : N_2(g)

The pro-degradants are
- introduced after 1 min
- reacted for **1 min**
- added at **0.5 wt%**

Fig. Influence of pro-degradant



- Benzene and PVC content can be lowered to 0.05 ppm.
- rPET was assessed using viscosity index (VI), chain-end titration, melt rheology, Fourier-transform infrared spectroscopy and differential scanning calorimetry (DSC).

Characterization of PET and rPET:

GC-MS/MS sensitive to part-per-million (ppm) **of impurities.**
Using Solid-Phase Micro-Extraction (**SPME**)

1. Desorption of Benzene	**150 / 200 °C** - 60 min
2. Pre-incubation of vial	30 °C - 5 min
3. Adsorption on fiber	30 °C - 20 min
4. Desorption in GC inlet	250 °C - 5 min

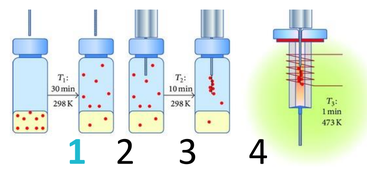
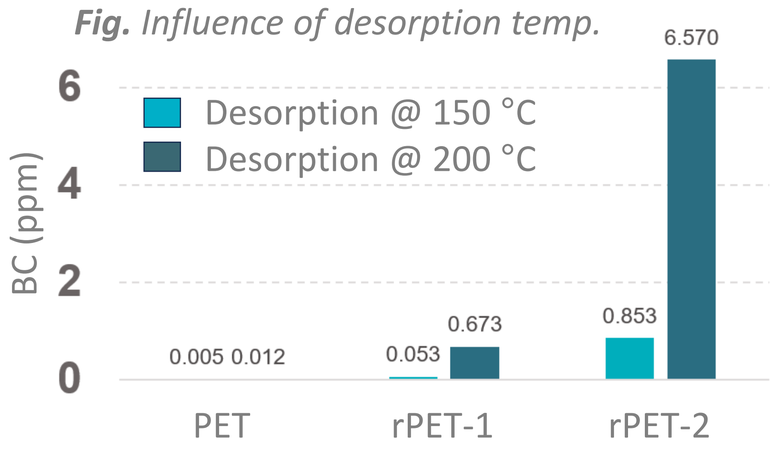
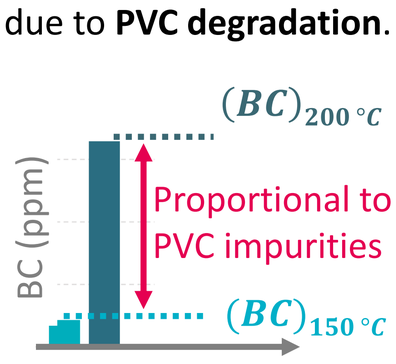


Fig. SPME steps

Fig. Influence of desorption temp.



Increasing the desorption temp. up 200 °C leads to drastic increase (up to 10x) in benzene content (**BC**) due to **PVC degradation**.



➔ Free benzene = $(BC)_{150\,°C}$
➔ PVC content can be estimated by :
PVC α $(BC)_{200\,°C} - (BC)_{150\,°C}$

Conclusions: improved rPET purity

- Benzene content ÷ by 10
- Fast reaction (< 1 min)
- VI of PET maintained
- Food contact ensured

PENDING PATENTED PENDING

*Patent application “Method for purifying a thermoplastic material by selective degradation of impurities”, **LU508013, 2024.***

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