A new system for the recovery and the recycling of thermoplastic polyurethanes (TPU) from ski boot equipment

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An ecological problem

- Raw materials
- Processing & assembling
- Skiboot product
- Lifetime
- Landfilling

→ A linear «cradle to grave» economy

→ 7 million of skiboot are annually destined to landfill and/or incenerinator

→ 10-15 kton of wastes annually generated
An ecological transition

Raw materials → Processing & assembling → Skiboot product → Lifetime → Endlife → Collection → Recycling processes

How switch from linear to circular lifecycle?
An ecological transition

The main recycling problems:

- It is difficult to **collect** the end-of-life skiboots.
- Skiboots have a **complex and variable** multi-material **composition**

How switch from linear to circular lifecycle?
An ecological transition

The main recycling problems:

- It is difficult to collect the end-of-life skiboots.
- Skiboots have a complex and variable multi-material composition.

Collaboration with Ski Rental Shoops

- They solve the problems of collection.
- They solve the variability of the skiboot composition (entry level/intermediate skiboots).
Skiboot composition  
*(intermediate and entry-level skiboots)*

- Inner boot (EVA) 24,9%wt.
- Straps (Velcro) 2,2%wt.
- Cuff (TPU) 22,3%wt.
- Shell (TPU) 30,2%wt.
- Buckles (steel and Al) 12,9%wt.
- Sole (TPU) 4,2%wt.
- Insole (PP) 2,7%wt.

M_{tot} = 2,256 kg  
56,7%wt. of TPU
Aims of the work

1) Investigating the recyclability of the TPU polymers in terms of:
   - ski-boot’s lifetime and state of wear
   - number of the recycling steps
   - weathering ageing

   → How much is recyclable the sorted TPU?

2) How can be TPU industrially sorted?
   → (Not treated here); spoiler: yes

3) Investigating the techno-economic profitability of the proposed recycling processes
   → The proposed recycling processes can be scaled-up?

4) Investigating the environmental impact of the proposed recycling processes
   → (Not treated here here); spoiler: yes
Scheme of the work (Lab-scale)

Ski rental shops

- Virgin (t0)
- 20 days lifetime (t20)
- 50 days lifetime (t50)

TPU Cuff and Shell

Other components

Grinder

TPU flakes

Testing

Weathering

Specimens

Injection molding

Recycling loops

Tensile test
Flexural test
TGA - DSC

UV

Thermal

Water

CORFU 2022 – 9th international conference on sustainable solid waste management, 15-17 June 2022
Tensile properties t0-t20-t50

The lifetime of the skiboot (t0-t20-t50) does not affect the tensile properties.
Flexural properties
t0-t20-t50

**Flexural Modulus [MPa]**

- TPU-Shell-t0
  - 300 ± 30

- TPU-Shell-t20
  - 330 ± 33
  - +31%

- TPU-Shell-t50
  - 350 ± 35
  - +8%

**Flexural Stress at 5% [MPa]**

- TPU-Shell-t0
  - 20 ± 2

- TPU-Shell-t20
  - 17 ± 1
  - -19%

- TPU-Shell-t50
  - 15 ± 1
  - -17%

**Flexural strength [MPa]**

- TPU-Shell-t0
  - 40 ± 4
  - -20%

- TPU-Shell-t20
  - 35 ± 3
  - -20%

- TPU-Shell-t50
  - 30 ± 3

**Table:**

<table>
<thead>
<tr>
<th></th>
<th>Flex modulus [MPa]</th>
<th>Flex stress at 5% [MPa]</th>
<th>Flex strength [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1-t0</td>
<td>226 ± 34</td>
<td>27,7 ± 2,7</td>
<td>41,3 ± 1,9</td>
</tr>
<tr>
<td>R1-t20</td>
<td>244 ± 31</td>
<td>22,3 ± 0,4</td>
<td>32,9 ± 2,1</td>
</tr>
<tr>
<td>R1-t50</td>
<td>297 ± 37</td>
<td>23,1 ± 0,7</td>
<td>33,0 ± 1,8</td>
</tr>
</tbody>
</table>

Used (t20 and t50) recycled (R1) TPUs have reduced flexural properties.
Aged specimens
t0-t20-t50

Water aging = samples are immersed in water for 24 hours and then frozen to simulate the melting/freezing cycles which ski-boots are subjected in the snow;
→ plasticizing effect : water molecules bonded with the ester polymer chains.

Oven aging = samples are placed in oven for 100 hours at 75 °C to accelerate the degradation of the polymer matrix:
→ hardening effect samples become stiffer and loose their ductility.

→ Water and thermal aging show opposite counterbalancing effects.
Recycling loop

Recycling of t0

Young Modulus [MPa]

Tensile Strength [MPa]

Elongation at break [%]

<table>
<thead>
<tr>
<th>Sample</th>
<th>E [MPa]</th>
<th>TS [MPa]</th>
<th>e,break [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1-t0</td>
<td>159 ± 14</td>
<td>44 ± 1</td>
<td>1046 ± 50</td>
</tr>
<tr>
<td>R2-t0</td>
<td>161 ± 2</td>
<td>43 ± 2</td>
<td>1143 ± 75</td>
</tr>
<tr>
<td>R3-t0</td>
<td>201 ± 8</td>
<td>37 ± 2</td>
<td>1075 ± 80</td>
</tr>
<tr>
<td>R4-t0</td>
<td>186 ± 7</td>
<td>26 ± 3</td>
<td>840 ± 139</td>
</tr>
</tbody>
</table>

t0 skiboots are recyclable up to three times
Recycling loop

Recycling of t50

t50 skiboots are recyclable up to two times
Conclusions

1) Tensile properties are not affected by the lifetime of the skiboot, while flexural properties are (slightly).

2) Accelerated weathering aging modify the mechanical behaviour of the TPU polymer but the overall properties result similar to untreated TPU as oven and water aging show opposite counterbalancing effects.

3) Among the different contributes (lifetime usage, weathering and recycling), the reprocessing is the one that most affect the mechanical properties of recovered TPU.

4) However, the properties of recycled TPU were overall satisfactory up to the 2th recycling step.
Techno-Economic Analysis

Collection $\rightarrow$ Grinder $\rightarrow$ Sorting $\rightarrow$ Triboelectric $\rightarrow$ Extrusion $\rightarrow$ Other component $\rightarrow$ Wastes

Approach 1: direct sell of sorted TPU flakes– no extrusion
Approach 2: extrusion of sorted TPU flakes with vTPU

Total polymers recovered = 78%wt.
### Techno-Economic Analysis

#### Grinder
- **PC**: 103 k€
- **Productivity**: 100 kg/h
- **Consumption**: 80 W/kg
- **Labor**: 1 pers./machine

#### Sorting
- **PC**: 350 k€
- **Productivity**: 500 kg, in/h
- **Consumption**: 3'150 W/kg
- **Labor**: 2 pers./machine

#### Extrusion
- **PC**: 195 k€
- **Productivity**: 150 kg/h
- **Consumption**: 400 W/kg
- **Labor**: 1 pers./machine

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**The plant is able to recycle up to 300k ski-boots for years (677 ton)**

- **Selling price of r-EVA**: 1,5 €/kg
- **Selling price of r-TPU**: 3,0 €/kg
- **vTPU content**: 0-50%wt.
- **vTPU cost**: 4,0 €/kg
- **Depreciation time**: 10 years

- **Electricity cost**: 0,1984 €/kWh
- **Waste tax**: 0,3 €/kg
- **Transports cost**: 0,32 €/(ton*km)
- **Labor cost**: 18 €/h
- **Taxes**: 24%
Techno-Economic Analysis

- **Total Investment Cost (TIC)**
  \[
  TIC (\text{€}) = \text{Direct Fixed Costs (DFC)} + \text{Working capital} + \text{Start up & validation}
  \]
  Required expenses needed to build-up the entire new recycling plant

- **Net Profit (P)**
  \[
  P(\text{€}) = \text{Revenues} - \text{Annual Operating Costs} - \text{Taxes} + (\text{Depreciation})
  \]
  \(P\) indicates if, a part from the TIC, the recycling processes are profitable or not

- **Net Present Value (NPV)**
  \[
  NPV (\text{€}) = \sum_{t=2}^{10} \frac{P_t}{(1 + d)^t} - TIC
  \]
  \(d = \text{discount rate} = 7\%
  \]
  NPV indicates if the **new recycling plant** is profitable in 10 years
The recycling processes are profitable when 20k ski-boots (0.3%) are recycled.

When 100k ski-boots are recycled (1.4%), the net profit is of 129k€.
The recycling processes are profitable when 30k ski-boots (0.3%) are recycled and P ranges between 13 k€ (vTPU=50%) and 23 k€ (vTPU=0%).

When 100k ski-boots are recycled (1.4%), the net profit ranges between 210 k€ (vTPU=50%) to 219 k€ (vTPU=0%).
The recycling plant is profitable when **70k ski-boots** (1.0%) are recycled.

**Techno-Economical Analysis**

**NPV (plant) - No extrusion**

<table>
<thead>
<tr>
<th>Recycled ski-boot [-] \times 10^4</th>
<th>NPV [k€]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>37 k€</td>
</tr>
<tr>
<td>4</td>
<td>100k ski-boots</td>
</tr>
<tr>
<td>6</td>
<td>461 k€</td>
</tr>
<tr>
<td>8</td>
<td>70k ski-boots</td>
</tr>
<tr>
<td>10</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td></td>
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</tbody>
</table>

**Total Investment Cost** \(\approx 1.0-1.2 \text{ M€}\)
Techno-Economical Analysis
NPV (plant) - Extrusion with vTPU

The recycling plant is profitable when 100k ski-boots (1.4%) are recycled and vTPU is <35% or when 110k ski-boots (1.6%) are recycled and vTPU is >35%.

Total Investment Cost ≈ 1.2-1.5 M€
Conclusions

The number of recycled ski-boots (input raw material) affects the economic profitability much more than the use (or not) of vTPU.

Recycling processes become profitable when 20-30 k ski-boots are collected (third-part processes) but an apposite recycling plant should be build-up only when at least 70k (in case of direct sell of rTPU) or 100-110 k ski-boots (in case of extrusion of rTPU with vTPU) are collectable.
Thank You For Your Attention.
ThermoGravimetric Analysis

t0-t20-t50

t20 and t50 have the TGA curve left-shifted of 5-10 °C as consequence of possible degradative phenomena
Flexural tests
(t0-t20-t50)
Flexural properties do not significantly decrease with the number of recycling steps.
Flexural properties

Flexural consecutive cycles t0-t20-t50

During the first 3-4 cycles TPU became stiffer and then it starts to lose flexural properties.
The Net Profit:
- >0 when 20k ski-boots (0.3%) are recycled
- =144k€ when 70k ski-boots (1%) are recycled
- =214 k€ when 100k ski-boots (1.4%) are recycled

The NPV:
- =37k€ when 70k ski-boots (1%) are recycled
- =461 k€ when 100k ski-boots (1.4%) are recycled

Total Investment Cost ≈ 1.1 M€
Techno-Economical Analysis
Approach 2: Extrusion of vTPU

**Total Investment Cost** ≈ 1.2-1.5 M€

The net profit:
- >0 when 30k ski-boots (0.4%) are recycled
- =144k€ when 70k ski-boots (1%) are recycled
- =214 k€ when 100k ski-boots (1.4%) are recycled

The NPV:
- >0 € when 110k ski-boots (1.6%) are recycled and vTPU<35%
- =461 k€ when 100k ski-boots (1.4%) are recycled
An ecological transition

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- Raw materials
- Processing & assembling
- Skiboot product
- Recycling processes
- Collection
- Lifetime
- Endlife

Recycling processes