Mechanical recycling of PE/PA6 – multilayer film waste – opportunities & limits

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BASF SE

partially a joint project of
Polyamides (PA) are officially classified as “non-recyclable materials”

The postulation of a general “non-recyclability” isn’t correct, because

- a certain amount of PA is dispersible in polyolefins
- higher PA – concentrations might be homogenized via compatibilization

Current trend of “elimination of PA” doesn’t consider fundamental benefits of PA:

- outstanding product performances in combination with
- real downgauging potentials,
- reduced consumption of necessary plastics raw materials,
- significantly improved shelf life and protection of food stuff

Here mechanical recycling is heavily promoted for the sake of mechanical recycling only, sustainable view is faded out!
What are the fundamental principles for our approach?

- Despite of a general incompatibility, Polyamides (PA) and Polyethylenes (PE) are dispersible and processable in a range of < 10% PA. (1)

- The PA – content in “post consumer” packaging waste in Germany is about < 2%(2) Such concentrations are directly recyclable by using suitable processing conditions.

- PA – contents of > 10% are dispersible by using sufficient compatibilizers, best efficiency of MAH – grafted polyolefin modifiers has been confirmed already. (3-5)

- The PA – part in mixed packaging waste stream contains significant amounts of PA 6/6.6 Copolyamides showing < 200°C additionally to PA6.

- Temperature profile for regranulation might be reduced from app. 240°C (PA 6) to a 210°C level (standard conditions for current recycling procedures).

- Preference of evaluation of a regranulation process without use of twin-screw extrusion devices as well as elimination of additional drying steps during processing of regranulates.

(1) Erfahrungswerte BASF SE, 2019 / 2020
(2) Wenigmann, S.; Chemical Recycling – The missing link to circular economy? Vortrag ZLV Film Symposium, Kempten 09/2019
(5) Jiang C.; Filippi S.; Magagnin P.; Reactive compatibilizer precursors for LDPE/PA 6 blends, part II; maleic anhydride grafted polyethylenes; Polymer 44, 8 (2411-2422) 2003
What has been done in detail? (Phase 1 – Focus to PA6)

- Reference: PE/PA6 – Multilayer films with 20% PA6 (Ultramid B40LN) as “worst case”, integration of compatibilizer already in original- (primary) film structures
- Regranulation (Standard NGR device)
- Analysis of morphologies of regranulates
- Processing of mono(blown)films (40µm) made from regranulates in semi-tech scale, dilution series with/without compatibilizer during blown film process
- Visual evaluation and analysis of mechanical properties of monolayer films
- Processing of multilayer(blown)films (70µm) using real production conditions, variations of PE/PA6 – regranulate as well as compatibilizer concentrations in core layer
- Visual evaluation and analysis of mechanical properties of multilayer films
Film structures

- **Trial 1.0 (Reference):** PE/PE/PE/PE/PE/PE/PE/PE/PE

- **Trial 1.1 (Reg A):** PE/PE/PE/tie/B40LN/tie/PE/PE/PE (20% B40LN*)

- **Trial 1.2 (Reg R):** PE/PE(incl. CompR)/PE/tie/B40LN/tie/PE/PE(incl. CompR)/PE (20% B40LN, 2 x 2.5% Retain 3000**) 

- **Trial 1.3 (Reg F):** PE/PE(incl. CompF)/PE/tie/B40LN/tie/PE/PE(incl. CompF)/PE (20% B40LN, 2 x 2.5% Fusabond E226***)

* Ultramid® B40LN = high viscosity (RV = 4,0), nuleated PA6, source: BASF SE
** & *** 2 different types of compatibilizers, source: Dow/DuPont
Regranulation technology

S Gran 95, NGR Recycling Machines, Austria
Combination of shredder/feeding unit with single screw extrusion device, up to 400 kg/h throughput, 210 - 240°C melt temperature, no additional drying step of regranulates
Morphologies of regranulate pellets made from PE/PA6 film waste

Compatibilizers in original film structures already generates well homogenized PE/PA6 – regranulates!
examples here = 80%PE/20%PA6 without (A) and with compatibilizers (R,F)
## Recipe overview I – Focus (Pre) - Compatibilization

<table>
<thead>
<tr>
<th>Trials</th>
<th>Reg A (%/PA)</th>
<th>Reg R (%/PA)</th>
<th>Reg F (%/PA)</th>
<th>PE Regranulate (%)</th>
<th>Compatibiliser F* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
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<td>100 / 20</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.2</td>
<td>-</td>
<td>100 / 20</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.3</td>
<td>-</td>
<td>-</td>
<td>100 / 20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.4</td>
<td>95 / 19</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>1.5</td>
<td>-</td>
<td>95 / 19</td>
<td>-</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>1.6</td>
<td>-</td>
<td>-</td>
<td>95 / 19</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>1.7</td>
<td>40 / 8</td>
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<td>-</td>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td>1.8</td>
<td>-</td>
<td>40 / 8</td>
<td>-</td>
<td>60</td>
<td>-</td>
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<td>1.9</td>
<td>-</td>
<td>-</td>
<td>40 / 8</td>
<td>60</td>
<td>-</td>
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<tr>
<td>1.10</td>
<td>50 / 10</td>
<td>-</td>
<td>-</td>
<td>47</td>
<td>3</td>
</tr>
<tr>
<td>1.11</td>
<td>-</td>
<td>50 / 10</td>
<td>-</td>
<td>47</td>
<td>3</td>
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<td>1.12</td>
<td>-</td>
<td>-</td>
<td>50 / 10</td>
<td>47</td>
<td>3</td>
</tr>
</tbody>
</table>

* Fusabond E226, all components mixed as salt & pepper blends prior to blown film process directly!
Morphologies I – Monolayer blown films I

PE/PA6 Blend 1.2 (pre-compatibilized Reg R)  PE/PA6 Blend 1.3 (pre-compatibilized Reg F)
Mechanical properties in comparison Ia (3 Basic recipes)

Monolayer 100% regranulate (MD*)

*MD = machine direction

Values (%)

<table>
<thead>
<tr>
<th>STRENGTH</th>
<th>ELONGATION (BREAK)</th>
<th>E-MODULUS</th>
<th>PUNCTURE (STRENGTH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Referenz PE 1.0</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>1.2</td>
<td>92.2</td>
<td>96.7</td>
<td>129.7</td>
</tr>
<tr>
<td>1.3</td>
<td>109.4</td>
<td>96.9</td>
<td>150</td>
</tr>
</tbody>
</table>

Regranulate A (80PE/20PA6) without compatibilizer (trial 1.1) not involved due to lack of processability!
Trials 1.2 + 1.3 contain already compatibilizers as part of original recipes!
Mechanical properties in comparison lb (3 Basic recipes)

Monolayer 100% regranulate (TD*)

*TD = transversal direction

Referenz PE 1.0 1.2 1.3

Regranulate A (80PE/20PA6) without compatibilizer (trial 1.1) not involved due to lack of processability!
Trials 1.2 + 1.3 contain already compatibilizers as part of original recipes!
# Recipe overview II – Dilution with/without compatibilizer

<table>
<thead>
<tr>
<th>Trials</th>
<th>Reg A* (%/ %PA)</th>
<th>PE Regranulate (%)</th>
<th>Compatibilizer F** (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>-</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>1.1</td>
<td>100 / 20</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>50 / 10</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td>3.2</td>
<td>37,5 / 7,5</td>
<td>62,5</td>
<td>-</td>
</tr>
<tr>
<td>3.2</td>
<td>25 / 5</td>
<td>75</td>
<td>-</td>
</tr>
<tr>
<td>1.4</td>
<td>95 / 19</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>4.2</td>
<td>50 / 10</td>
<td>45</td>
<td>5</td>
</tr>
<tr>
<td>1.10</td>
<td>50 / 10</td>
<td>47</td>
<td>3</td>
</tr>
<tr>
<td>4.3</td>
<td>37,5 / 7,5</td>
<td>57,5</td>
<td>5</td>
</tr>
<tr>
<td>4.4</td>
<td>25 / 5</td>
<td>70</td>
<td>5</td>
</tr>
</tbody>
</table>

* 20% B40LN  
** Fusabond E226  

All components mixed as salt & pepper blends prior to blown film process directly!

- Weber 30 aircooled blown film line  
- 30mm screw, L/D = 25  
- Die diameter 50mm  
- Lay flat 350 mm,  
- Temperatures 235°C/240°C
Morphologies II – Monolayer blown films II (Dilution trials, excerpts)

**Monolayer 3.2 = 7,5% B40LN**

**Monolayer 3.3 = 5% B40LN**

* 5% Fusabond E226

**Monolayer 1.4* = 19% B40LN**

**Monolayer 4.2* = 10% B40LN**

without compatibilizer
Mechanical properties in comparison IIa -
(Dilution trials, without compatibilizer)

Monolayer 100% regranulate (MD*)

*MD = machine direction

All components mixed as salt & pepper blends prior to blown film process directly!
Mechanical properties in comparison IIb - (Dilution trials, without compatibilizer)

**Monolayer 100% regranulate (TD*)**

<table>
<thead>
<tr>
<th>Property</th>
<th>Referenz PE 1.0</th>
<th>3.1 (10%PA6)</th>
<th>3.2 (7.5%PA6)</th>
<th>3.3 (5%PA6)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>STRENGTH</strong></td>
<td>100</td>
<td>66</td>
<td>77</td>
<td>82</td>
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<tr>
<td><strong>ELONGATION</strong> (BREAK)</td>
<td>100</td>
<td>87</td>
<td>96</td>
<td>102</td>
</tr>
<tr>
<td><strong>E- MODULUS</strong></td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>96</td>
</tr>
<tr>
<td><strong>PUNCTURE</strong> (STRENGTH)</td>
<td>100</td>
<td>97</td>
<td>101</td>
<td>97</td>
</tr>
<tr>
<td><strong>ELMENDORF TEAR</strong></td>
<td>100</td>
<td>134</td>
<td>122</td>
<td>119</td>
</tr>
</tbody>
</table>

*TD = transversal direction

All components mixed as salt & pepper blends prior to blown film process directly!
Mechanical properties in comparison IIIa - (Dilution trials, with compatibilizer)

All components mixed as salt & pepper blends prior to blown film process directly!
All trials were processed using 5% Fusabond E226, except trial 1.10 with 3% only!
Mechanical properties in comparison IIIa - (Dilution trials, with compatibilizer)

Monolayer 100% regranulate (TD*)

Values (%)

STRENGTH  ELONGATION (BREAK)  E-MODULUS  PUNCTURE (STRENGTH)  ELMENDORF TEAR

Referenz PE 1.0  1.4 (19%PA6)  4.1 (15%PA6)  1.10 (10%PA6*)  4.3 (7.5%PA6)

*TD = transversal direction

All components mixed as salt & pepper blends prior to blown film process directly!
All trials were processed using 5% Fusabond E226, except trial 1.10 with 3% only!
### Recipe overview III – PE/PA6 – regranulates in multilayer films

- **Reference 1_1:** PE(12,5µm)/PE(45µm)/PE(12,5µm)
- **All other trials:** PE(12,5µm)/PE + Regranulate(45µm)/PE(12,5µm)

<table>
<thead>
<tr>
<th>Trials</th>
<th>PA 6 (B40LN*, %)</th>
<th>Reg A (%)</th>
<th>Reg A** (%)</th>
<th>Reg R (%)</th>
<th>Reg F (%)</th>
<th>PE (%)***</th>
<th>Comp.R**** (%)</th>
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<tbody>
<tr>
<td>2</td>
<td>6,4# (4###)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>93,6</td>
<td>-</td>
</tr>
<tr>
<td>4b</td>
<td>6,4# (4###)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>92,0</td>
<td>1,6</td>
</tr>
<tr>
<td>6b</td>
<td>-</td>
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<td>78# (10###)</td>
<td>-</td>
<td>-</td>
<td>20,0</td>
<td>2,0</td>
</tr>
<tr>
<td>6c</td>
<td>-</td>
<td>-</td>
<td>98# (12,5###)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2,0</td>
</tr>
<tr>
<td>18b</td>
<td>-</td>
<td>32# (4###)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>68,0</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>32# (4###)</td>
<td>-</td>
<td>68,0</td>
<td>-</td>
</tr>
<tr>
<td>22</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td>32# (4###)</td>
<td>68,0</td>
<td>-</td>
</tr>
</tbody>
</table>

* High viscosity, nucleated PA6 pellets, salt & pepper blend, added during blown film process
** Basic mix (PE80/PA20), regranulated using a 2nd machine (NGR tech center)
*** Basic blend LLDPE70/LDPE30, pure PE reference
**** Retain 3000 compatibilizer, salt & pepper blend, added during blown film process
# PA6 or PE/PA6 regranulate in core layer, respectively
## PA6 content in total film structure

- Varex II 3 – layer aircooled blown film line
- lay flat 1700 mm,
- melt temperature of 250°C in core layer
- 400 kg/h throughput
Morphologies III – Multilayer films with PE/PA6 regranulate content

Multilayer 18b = 6.4% PA 6 in core

Multilayer 6b = 15.6% PA 6 in core, 2%R

Multilayer 22 = 6.4% PA in core, 1.6% F

Multilayer 6c = 19.6% PA 6 in core, 2%R

Multilayer 1_1 = PE Reference
Mechanical properties in comparison IVa - Multilayer films (Excerpts)

Multilayer, regranulate in core layer (MD*)

* MD = machine direction

Values (%)

<table>
<thead>
<tr>
<th></th>
<th>1_1 PE ref.</th>
<th>18b (6,4%B40LN)</th>
<th>22 (6,4%B40LN)</th>
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<td>STRENGTH</td>
<td>100</td>
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<td>100</td>
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<td>ELONGATION</td>
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<td>88</td>
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<tr>
<td>(BREAK)</td>
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<td>100</td>
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<td>E-MODULUS</td>
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<tr>
<td>PUNCTURE</td>
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<tr>
<td>(STRENGTH)</td>
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<td>107</td>
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<tr>
<td>ELMENDORF TEAR</td>
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<td>110</td>
</tr>
</tbody>
</table>

Values (%)

<table>
<thead>
<tr>
<th></th>
<th>6b (15,6%B40LN)</th>
<th>6c (19,6%B40LN)</th>
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<tbody>
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<tr>
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<tr>
<td>(BREAK)</td>
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<td>E-MODULUS</td>
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<td>136</td>
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<tr>
<td>PUNCTURE</td>
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<td>(STRENGTH)</td>
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<td>107</td>
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<tr>
<td>ELMENDORF TEAR</td>
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<td>76</td>
</tr>
</tbody>
</table>

PE/PA Recycling study – Dr. R.-E. Gruetzner, BASF SE 01/2021
Mechanical properties in comparison IVb - Multilayer films (Excerpts)

Multilayer, regranulate in core layer (TD*)

* TD = transversal direction

Values (%)

<table>
<thead>
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<th>STRENGTH</th>
<th>ELONGATION (BREAK)</th>
<th>E-MODULUS</th>
<th>PUNCTURE (STRENGTH)</th>
<th>ELMENDORF TEAR</th>
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<tbody>
<tr>
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</tr>
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<td>18b (6,4%B40LN)</td>
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<td>93</td>
<td>125</td>
<td>101</td>
<td>122</td>
</tr>
<tr>
<td>22 (6,4%B40LN)</td>
<td>93</td>
<td>87</td>
<td>135</td>
<td>107</td>
<td>88</td>
</tr>
<tr>
<td>6b (15,6%B40LN)</td>
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<td>61</td>
<td>121</td>
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<td>95</td>
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<tr>
<td>6c (19,6%B40LN)</td>
<td>60</td>
<td>82</td>
<td>137</td>
<td>99</td>
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</tr>
</tbody>
</table>

PE/PA Recycling study – Dr. R.-E. Gruetzner, BASF SE 01/2021
**Virgin blend**

Dosing of PA6 granules to PE (with & without compatibilizer)

| 70% 5056G | 63,6% GM8090 | 70% 5056G |
| 30% 310E | 30% 310E | 30% 310E |
| 6,4% B40L |

- **Very bad optic due to strong inhomogeneities**

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**Secondary Film**

**Basic trial**

| 70% 5056G | 62 % GM8090 | 70% 5056G |
| 30% 310E | 30 % 310E | 30% 310E |
| 6,4% B40L | 1,6% Retain 3000 |

- **Significant better film optic and homogeneity**
- **BUT still**
  - Strong spiral flow lines / defects
  - Elongate defects / marks
- **Higher level of Retain has no influence**
  - (3,2% instead of 1,6%)
PE/PA6 – regranulates in core layer
Dosing of PE/PA6 - regranulates to PE (with & without compatibilizer)

- Strong inconsistencies (looks like orange peel), but
- better dispersed compared to virgin pellet basics
- Strong spiral flow lines

Taken from a presentation of
WINDMÖLLER & HÖLSCHER

Secondary Film

- Good film optics & quality
- No spiral flow marks / lines
- No difference (subjective) between industrial (BASF) and tech center (NGR) regranulates
PE/PA6 – regranulates in core layer
Dosing of PE/PA6 – regranulates to PE (pre-compatibilized recipes)

70% 5056G  48% GM8090  70% 5056G
30% 310E  20% 310E  30% 310E
32 % Regranulate

Retain 3000 vs Fusabond E226
Good film optics using both compatibilizers

- No significant difference in subjective film optics
- No significant difference detected by OCS gel counter system
- Higher gel level of industrial regranulate with Retain in primary film

Taken from a presentation of WINDMÖLLER & HÖLSCHER

PE/PA Recycling study – Dr. R.-E. Gruetzner, BASF SE 01/2021
PE/PA6 – regranulates in core layer

Influence of dosing location (time) of compatibilizer

Subjective film optics are good for all three samples with Retain.

Film optics are independent of dosing time of compatibilizer.

Gel level for all dosing points of Retain is similar to reference film.

Taken from a presentation of WINDMÖLLER & HÖLSCHER

Secondary Film
Major conclusions

- PE/PA6 – blends containing < 10% PA6 are processable without any compatibilizer, the range of 5 - 8% PA6 – content has been confirmed as particularly sufficient.
- PE/PA6 – blends containing =/> 10% PA6 need compatibilizer for efficient recovery.
- Addition of MAH - grafted polyethylenes up to 5% has been confirmed as sufficient homogenization method for PE/PA6 – blends with up to 20% PA6 content.
- Compatibilizers might be added:
  - Into original- (primary) multilayer film structures (as functional layer)
  - During regranulation
  - During final processing (here films manufacturing)
- A temperature profile of about 240°C is recommended for PE/PA6 - blends.
- Reduced regranulation temperatures down to app. 210°C are possible.
- PE/PA6 – regranulates produced using standard single screw machinery are process-sable to monolayer films as well as integrated part of multilayer film structures showing acceptable visual and mechanical performances.
What is in progress or coming next, respectively?

- Reproduction of major conclusions for a 70%PE/30%PA6- multilayer film structure, dilution series using an industrial polyolefin recyclate reference, optimization of temperature profiles (joint project with cyclos-HTP) (all trials finished 12/2020)

- Evaluation of PE/PA6 - and PE/CoPA – blends according to Recycclass protocol (joint project with Dow & PRE) (trials starting 01/2021)

- Integration of EVOH – containing barrier film structures (film & regranulation trials done in 01/2021) as well as representative laminates

- Optimization of processing conditions, e.g.
  - Necessary drying?
  - Processing temperatures (target: 210- max. 220°C)
  - Concentrations of compatibilizer

Fundamental target is a general acceptance / re-classification of (mechanical) recyclability of Polyamides in post consumer packaging waste stream according to real material types and – concentrations.