

Mechanisches Recycling PolyAmid-haltiger Mehrschichtfolien

Mechanical Recycling of PolyAmide-containing
Multilayer Films

Dr. Rolf-Egbert Gruetzner, BASF SE
ZLV Fokustage 15.9. + 16.9.2021

BASF zu Gast bei
den ZLV-Fokustagen

- Status Quo of Polyamide acceptance – Past
- BASF evaluations in a nutshell
- Independent PA 6/PE multilayer film study carried out by cyclos-HTP
- Conclusions
- Status Quo of Polyamide acceptance – Update

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Insufficient info pushed public / legislation opinions

3. Appendix 3: Overview of packaging groups/sorts and material-specific recycling incompatibilities

Group/sort	Incompatibilities
Film and PE-LD	water-insoluble adhesive applications in combination with wet-strength labels, PA barriers, PVDC barriers, non-polymer barriers (excluding SiO ₂ /Al ₂ O ₃ /metallisations), non-EVOH barriers
Rigid PE	Silicone components; components of foamed non-thermoplastic elastomers; water-insoluble adhesive applications in combination with wet-strength labels; PA barriers; PE-X components, PVDC barriers; non-PO plastics with a density of < 1 g/cm ³
Rigid PP	Silicone components; components of foamed non-thermoplastic elastomers; water-insoluble adhesive applications in combination with wet-strength labels; PA barriers; PVDC barriers; non-PO plastics with a density of < 1 g/cm ³

Packaging Preferred Materials & Formats Guidelines 2020.

date: 13/02/20

Red Not to be used as customers cannot easily recycle (UK)		Amber When functional requirements mean green materials are not an option	Green Preferred for UK recycling via kerbside or store	
Materials Compostable/Bio degradable Oxy/Oxo Degradable PLA Polystyrene PVC PVdC (incl. layer within Complex Laminates) Plywood and MDF Water Soluble plastics	Formats & Designs Black Plastic* Composite Drums Expanded/Foamed/Density Modified Plastics Paper/board coated or laminated on both sides Glitter *Brands may choose to use black plastic for drink bottle caps	CONTROLLED USE: CONTACT THE PACKAGING TEAM FOR APPROVAL packaging.team@tesco.com	Rigid Materials Glass (clear or of light colour) PET HDPE/LDPE pp** Steel & Aluminium Cardboard Flexible Materials Paper Glassine PE (recyclable at front of store)	Formats & Designs Cardboard with plastic; Max 15% plastic, one side of board only and be easily separated Mono lidding film matched to tray material when permanently attached Glass colour; Clear/Light colour preferred
		Materials Non PE Flexible film incl. OPP Foiled paper New material innovations	Formats & Designs Beverage Cartons Multilayer Films/Complex Laminates Shrink sleeves (perforated, include messaging to remove, max coverage 40%)	

Underlined denotes red material/format added in 2020 (Production to cease by end of 2020)

**PP is widely recyclable, however may have a packaging tax implication for food grade if recycled content cannot be included



Excerpt from „Minimum standard for determining the recyclability of packaging subject to system Participation pursuant to section 21 (3) VerpackG“ of Stiftung Zentrale Stelle Verpackungsregister, Germany 2020

VI. Anhang Übersicht zu den gängigsten Verpackungsmaterialien

Barriere- und Siegelmaterialien

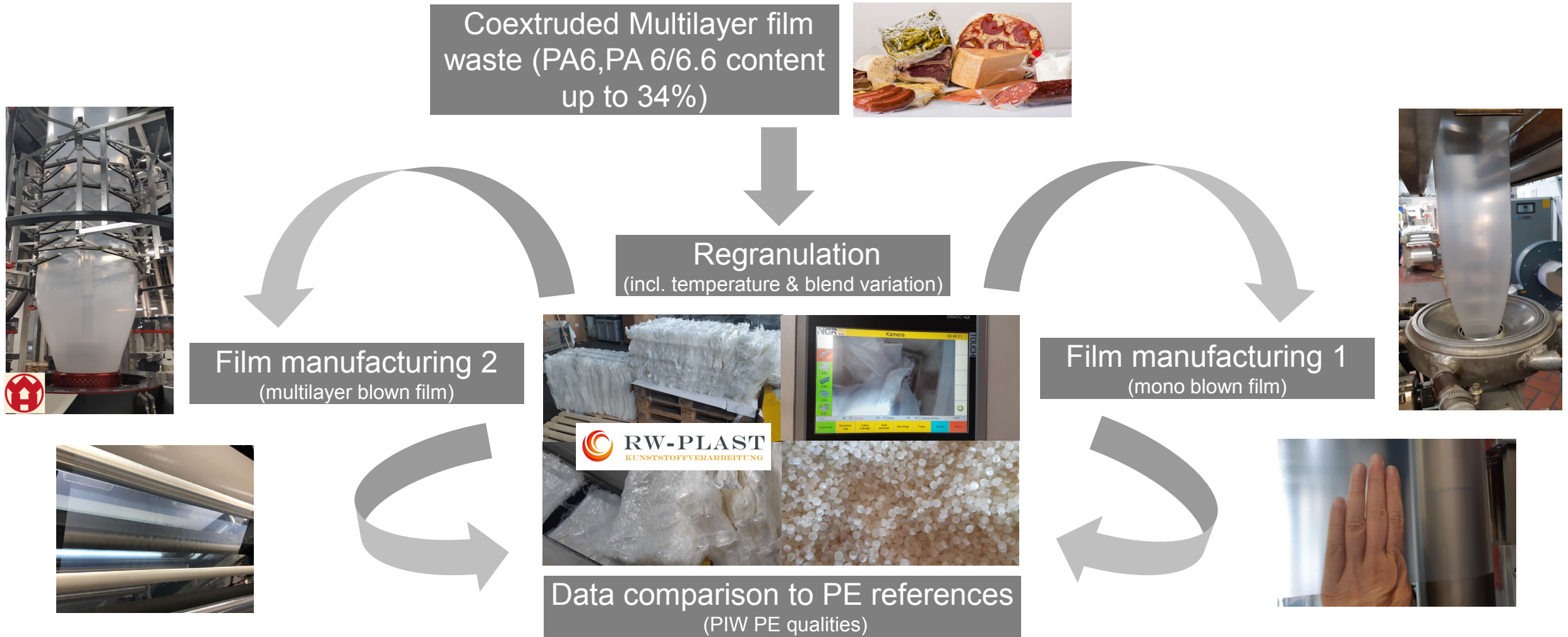
Bezeichnung	*	Erscheinungsbild des Ausgangsmaterials (d.h. ungefärbt bzw. unlackiert)	Mechanische Eigenschaften	Barriere Eigenschaften			Verwendung
				H ₂ O	O ₂	CO ₂	
<u>PA</u> Polyamid 6 und Polyamid 12	✗	• Transparent bei geringer Wandstärke	• Steif • Flexibel und dehnbar	-	-	-	Getränkeflaschen, thermogeformte Schalen, auch als Deckelfolie
<u>EVOH</u> Ethylenvinylalkohol Copolymer	✓	• Transparent bei geringer Wandstärke	-	bis ○	✓	✓	Barriere-Schicht in PP- oder PE-Verpackungen (Flaschen, Dosen, Schalen, etc.)

Excerpt from „Leitfaden für nachhaltigere Verpackungen, Version 2.0“ Aldi / Reclay Group, Germany 2020



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What has been investigated ?



partially a joint project



Film structures (example PA 6)

- **Trial 1.0 (Reference): PE/PE/PE/PE/PE/PE/PE/PE/PE**
- **Trial 1.1 (StructureA): PE/PE/PE/tie/B40LN/tie/PE/PE/PE (20% B40LN*)**
- **Trial 1.2 (StructureR): PE/PE(incl. CompR)/PE/tie/B40LN/tie/PE/PE(incl. CompR)/PE (20% B40LN, 2 x 2,5% Retain 3000**)**
- **Trial 1.3 (StructureF): 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**

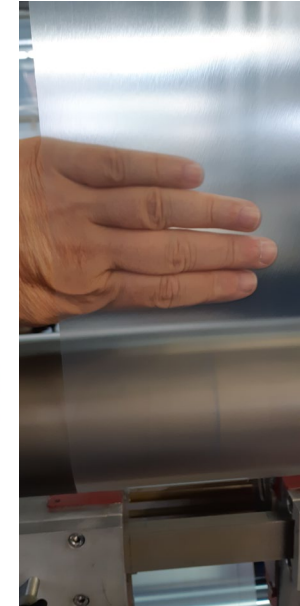
PA* concentrations < 10% are dispersible in a polyethylene stream w/o using compatibilizers



- PA*/PE pellet mix (PA*: 5-8%)
 - NO compatibilizer
 - Temperature range 215-240°C
 - NO additional compounding
 - NO additional drying



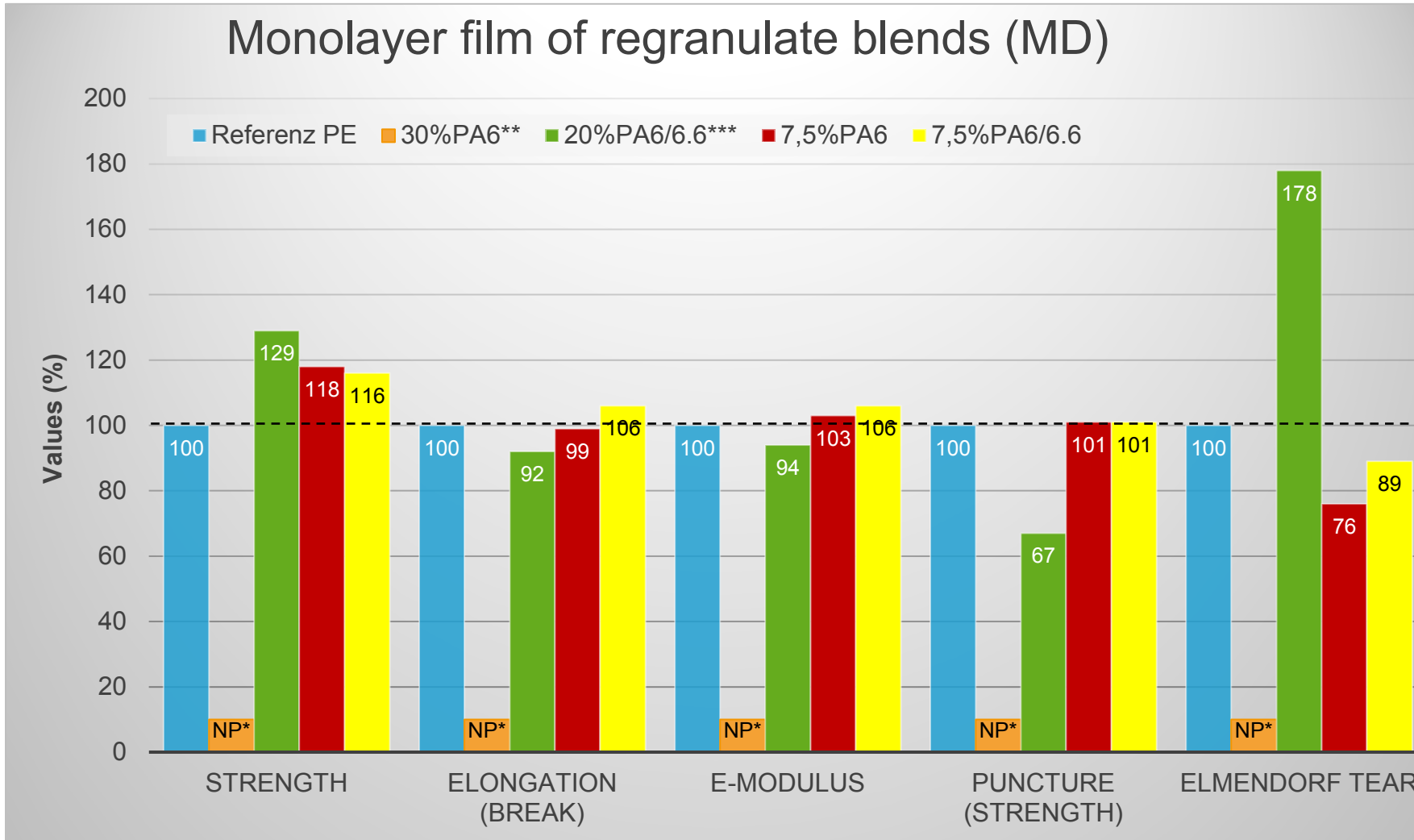
Direct processing of regranulate to 2nd blown film



Transparent films showing reasonable mechanical performance (mono-/ multilayer films)

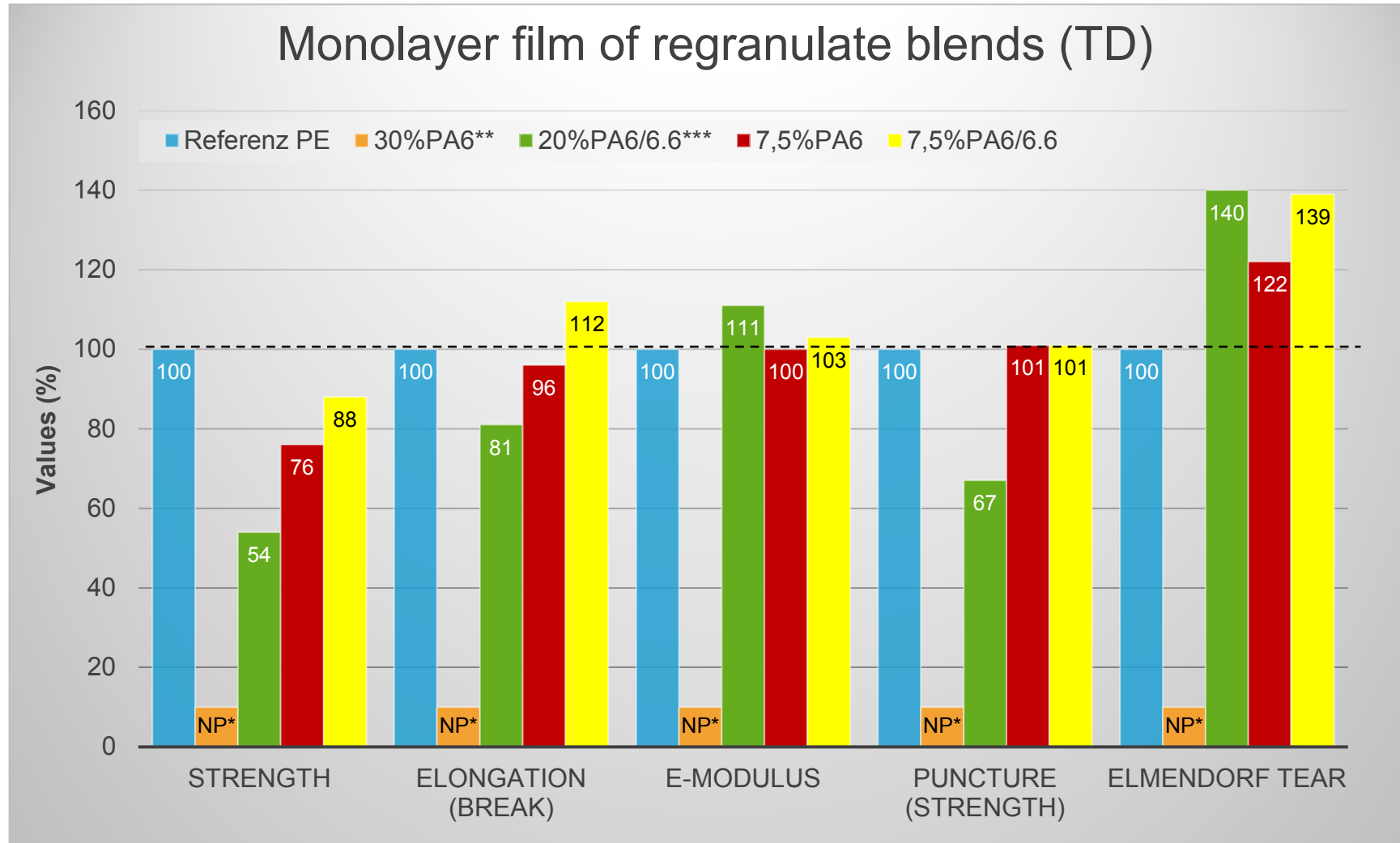
* PA 6 (e.g. Ultramid® B40LN) or PA 6/6.6 (e.g. Ultramid® C33, C40L or C37LC)

Comparison of mechanical properties in machine direction (MD) (Dilution w/o compatibilizer)



*NP = not processable
 **PA 6 = Ultramid® B40LN
 ***PA 6/6.6 = Ultramid® C40L
 All components mixed as salt & pepper blends prior to blown film process directly!!

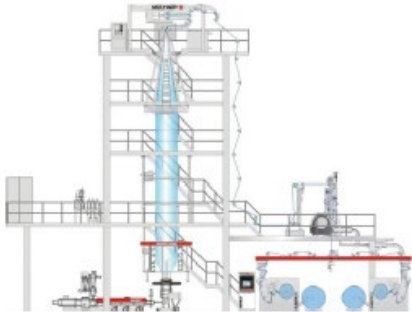
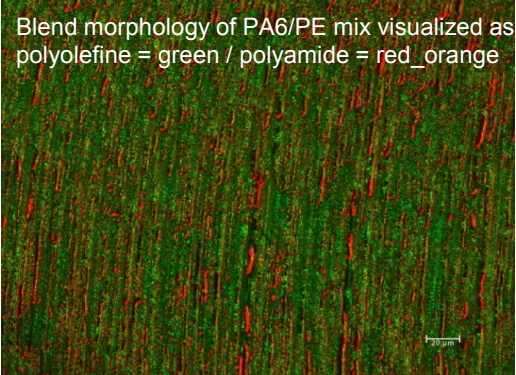
Comparison of mechanical properties in transversal direction (TD) (Dilution w/o compatibilizer)



*NP = not processable
 **PA 6 = Ultramid® B40LN
 ***PA 6/6.6 = Ultramid® C40L
 All components mixed as salt & pepper blends prior to blown film process directly!!

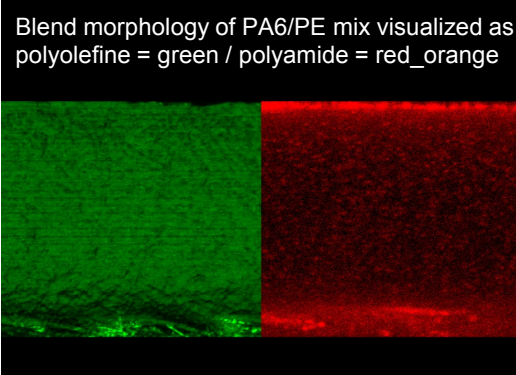
Compatibilization offers additional options for utilizing PA*/PE waste blends with PA* concentrations > 10% in a polyethylene stream

PA*/PE mix pur (pellet, 20% PA6)

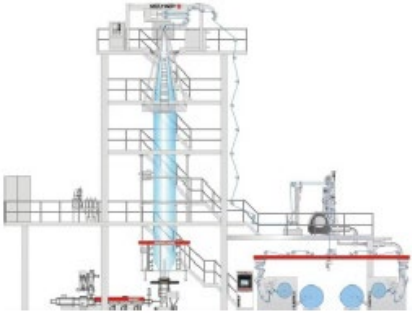
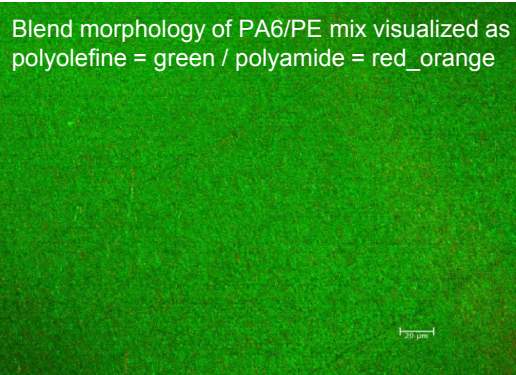


Compatibilizer added as **dry blend** during 2nd blown film process

Monolayer PA*/PE blown film

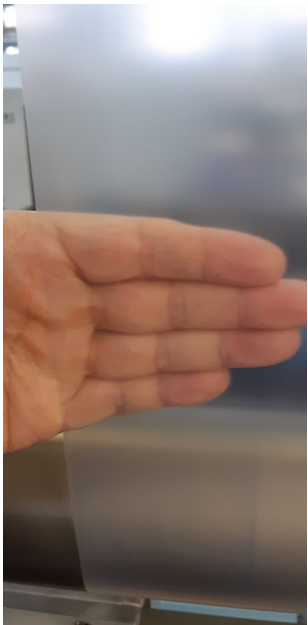
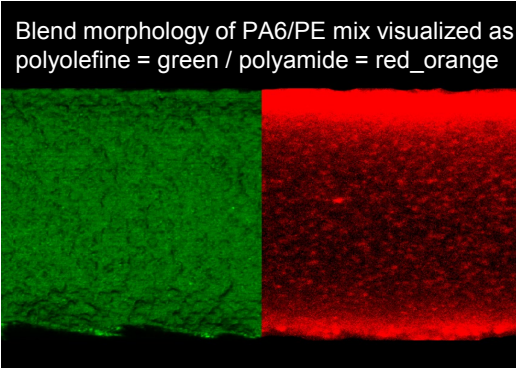


PA*/PE mix, pre-compatible (pellet, 20% PA6)



Direct processing of pre-compatible PIR during 2nd blown film process

Monolayer PA*/PE blown film



Transparent films showing reasonable mechanical performance (mono-/multilayer films)

* PA 6 (e.g. Ultramid® B40LN) or PA 6/6.6 (e.g. Ultramid® C33, C40L or C37LC)



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✓ **Targets of this project:**

- Investigation of the effects of PA6 (most critical PA grade) on the relevant properties of recyclates in LDPE film recycling
 - PA6 is incorporated **as coextruded layer with tie layers** in a LLDPE/LDPE film
 - Additional tests of films with PA6 and a commercial **compatibilizer** blended in PE
- Tests of the reference applications for LDPE recyclates:
 - Blown films
 - Injection moulding

→ **Assessment of PA6 as “Recycling Compatible” or “Recyclable” in LDPE films (by demand with use of a compatibilizer)**

✓ **Reference Processes**

Relevant Processes in the corresponding Recycling Path incl. **Recyclate Applications**

✓ **Reference Material**

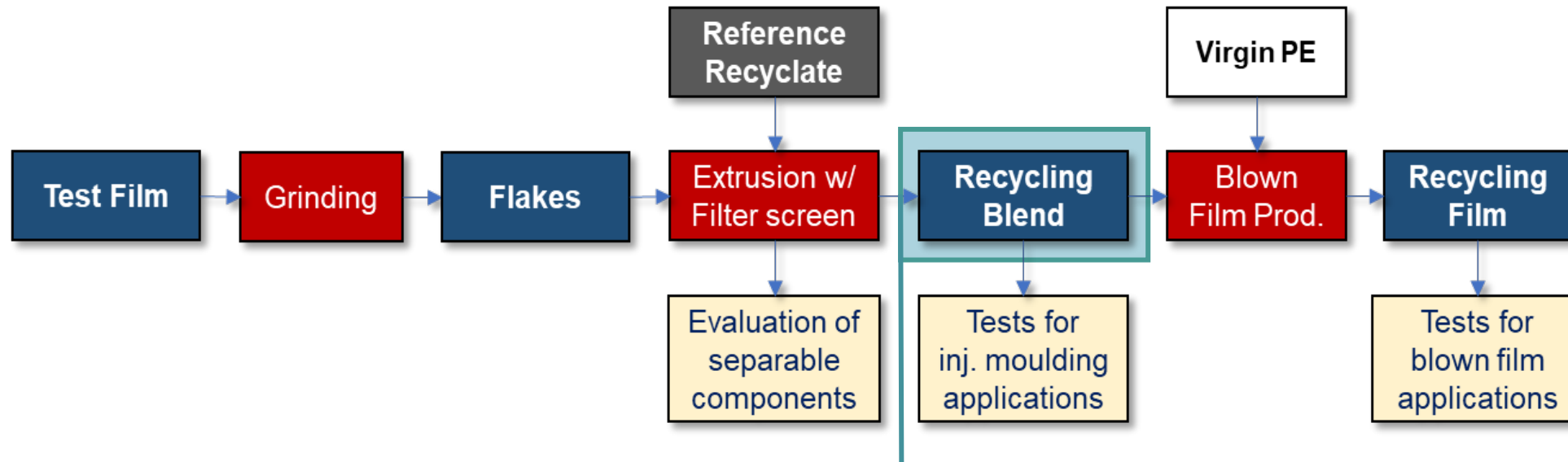
Commercial PCR recyclate commonly used for the same reference applications in the Recycling Path

✓ **Sample**

Packaging/Material containing a component with an **unknown recycling compatibility**



Recycling Application Compatibility Test for PE-based Flexible Packaging (CHI-C8-PEF-1)



Assessment of Recycling Blends *against Reference material*:

- CHI5** “Realistic Scenario” for the concentration of a packaging material in the recycling stream = **5% Sample** + **95% Reference** → **Compatibility of Packaging or Material?**
- CHI30** “Worst Case Scenario” for the concentration of a packaging material in the recycling stream = **30% Sample** + **70% Reference** → **100% Recyclability of Packaging ?**
- REF** Commercial **PCR Recyclate** from the recycling stream

Multilayer Blown Films produced at Windmüller & Hölscher

7 layer film structures:

FB0 – PE / PE / PE / PE / PE / PE / PE (100 µm)

FB1 – PE / Tie layer / **PA6** / Tie layer / **PA6** / Tie layer / PE

FB2 – PE + **Comp** / Tie layer / **PA6** / Tie layer / **PA6** / Tie layer / PE + **Comp**

“Recycling-critical” materials to be tested:

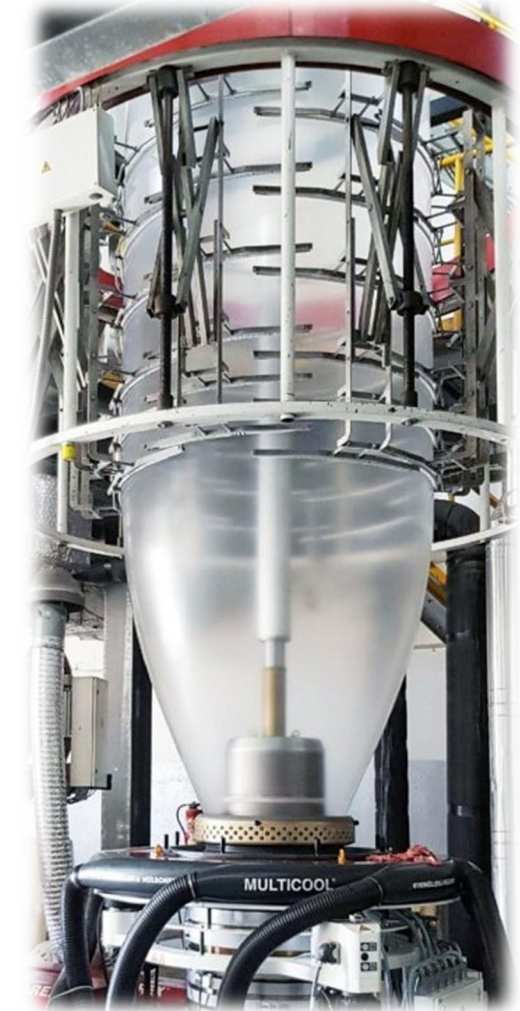
LDPE-based film with **30% PA6** and **15% tie layer resin ***

LDPE-based film with **15% PA6** and **7.5% tie layer resin ***

LDPE-based film with **30% PA6** and **15% tie layer resin *** and **5% Compatibilizer ****

** Maleic anhydride grafted PE (Standard grade for PA/PE coextrusion)*

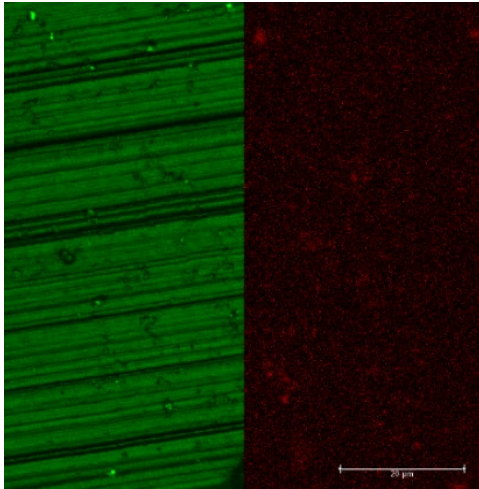
*** Maleic anhydride grafted PE (high MAH content)*



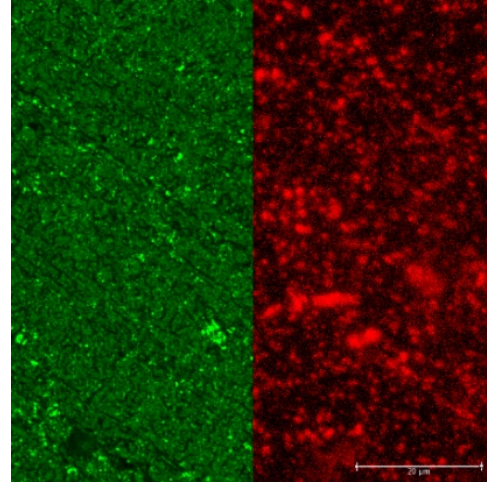
Morphology of Regranulate pellets after Regranulation on a NGR line



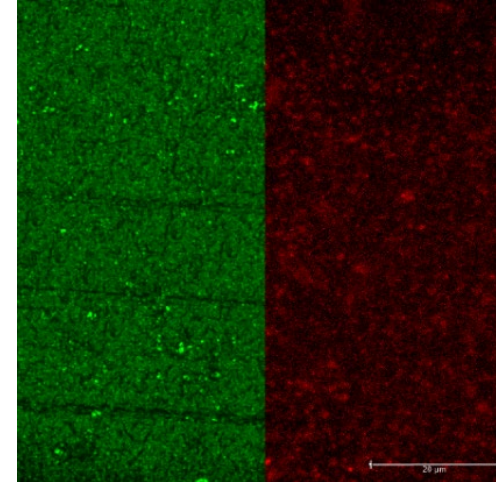
Regranulate,
100% PE reference



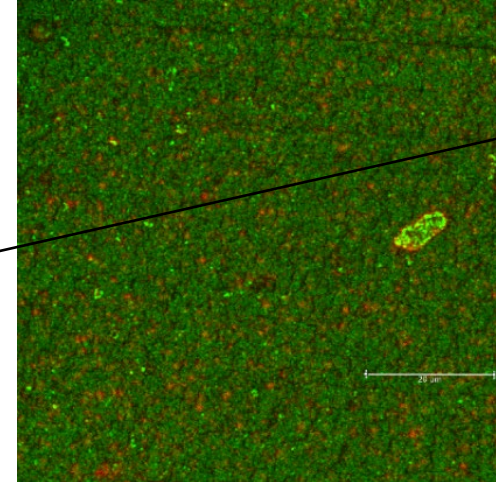
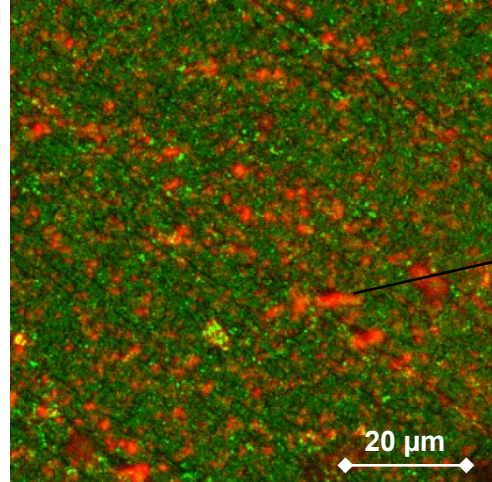
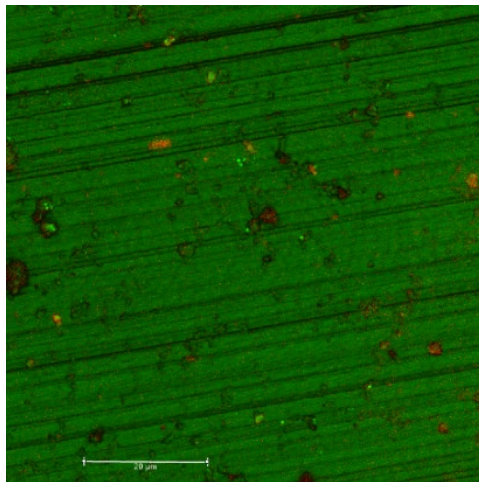
Regranulate w/
30% PA6, 15% Tie



Regranulate w/
30% PA6, 15% Tie,
5% Compatibilizer



Pre-compatibilization generates a **more homogeneous morphology** in comparison with 30% PA6 without compatibilizer



PA phases up to 10 µm

Reflection/Fluorescence microscopy (CLSM) pictures with kind permission by Dr. R.-E. Gruetzner, BASF SE 02/2021

Application Test for Blown Films



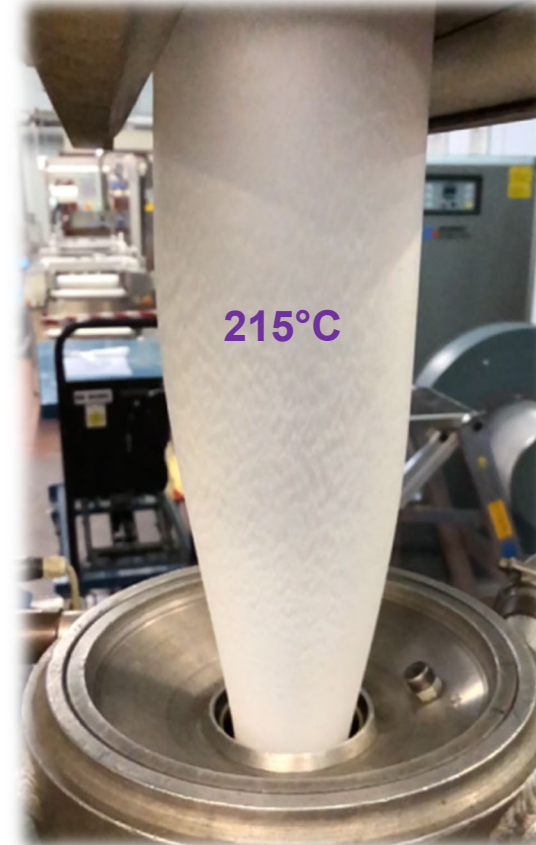
- Recyclate materials not dried !
- 50% virgin LD/LLDPE added for each film (Standard in industry)



5% PA, no Comp, 215°C



15% PA, 215°C

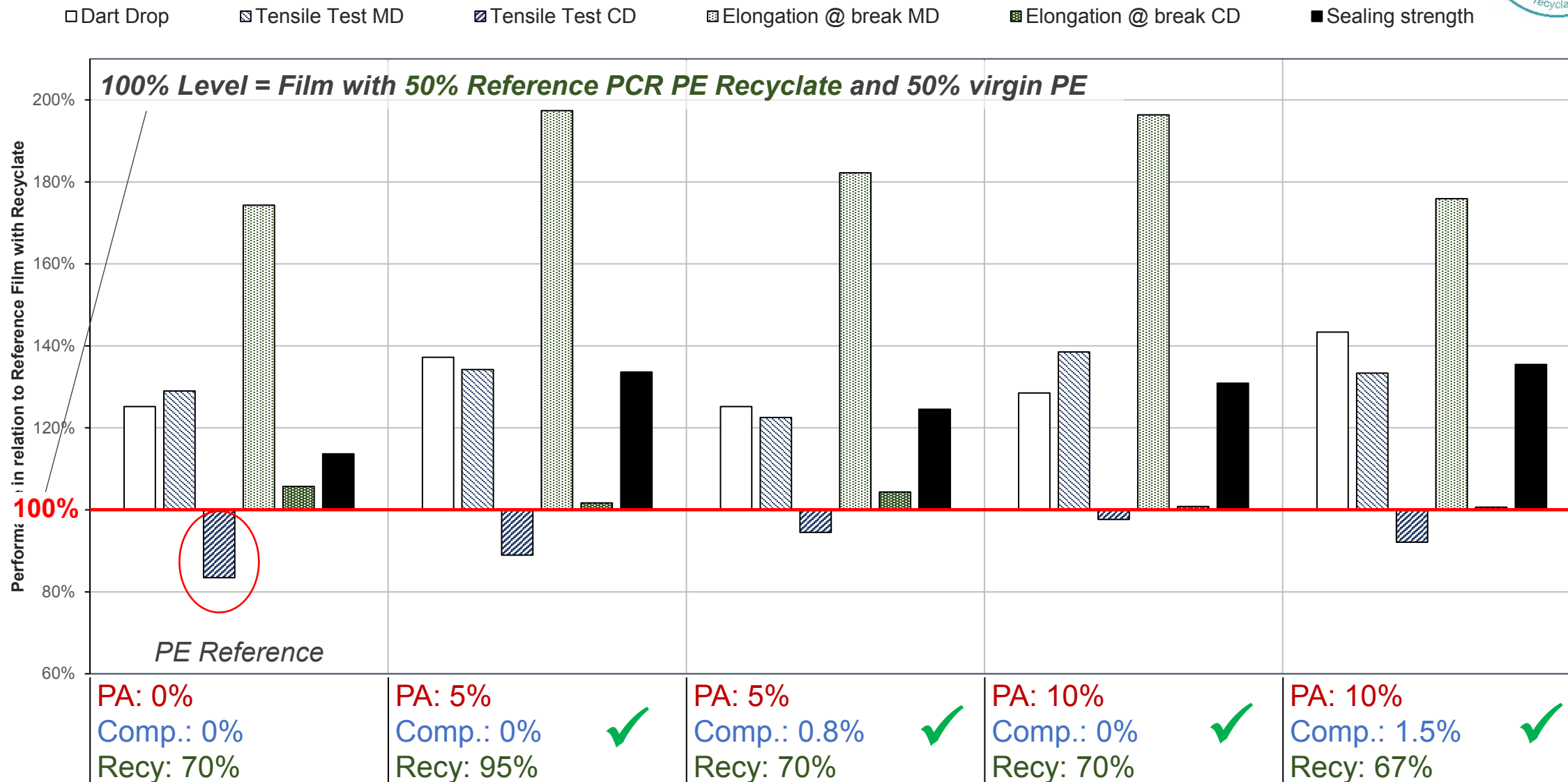


15% PA, 2.5% Comp.



Blown Film Application Tests – Mechanical and Sealing Properties

Blown Films made of 50% Recyclates and 50% virgin PE - Mechanical and Sealing properties





1. Films sealed with seam width of 2 - 4 mm
2. Filled with 1.3 L of water (with 16 cm seam length and 20 cm fill height)
3. Test duration: min. 10 minutes
4. Count the number of drops per minute due to leakages in the seam
5. Test is passed with < 2 drops per minute

All Sample Films
passed the test ✓




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Major conclusions

- PE/PA* waste mixtures are recyclable with PA* contents of < 10% **without using compatibilizers**
- Excellent PA* distribution and performance of recycled blends found using up to 7,5% PA*
- Compatibilizers are an efficient way to consistent PE/PA* mixtures with PA* contents of >> 10%
- Compatibilizers might be incorporated
 - already in original multilayer film structures (pre – compatibilization)
 - during regranulation by using standard single screw machinery
 - by adding as individual component on final processing (here film manufacturing) step
- While PE/PA6 films need a regranulation temperature of 220-240°C, realistic PA blends in packaging streams (PA6 + several lower melting CoPolyamides) are processable at about 210°C
- **NO drying steps** were necessary during our trials
- It is possible to use PE/PA* mixtures for manufacturing of mono-layer and multilayer structures, using highly concentrated PE/PA* mix core layers, showing sufficient mechanical and optical properties while using standard single screw extrusion equipment !

* including PA 6 (Tmelt 215-220°C) and different CoPolyamides (Tmelt 182-200°C) in coextruded multilayer structures

Status	Categorization of PA6 according to CHI standard 	CHI Assessment of a Packaging structure Example: PE film with 10% PA6 + ≥ 5% Tie layer	Material (PA6) according to ZSVR Minimum Standard
Current	CAT 3 <i>(PA in any structure)</i>	Not recyclable (0%)	Contaminant / Incompatible <i>(“PA layers”)</i>
<u>Future</u> (Based on results)	CAT 2 <i>(PA6 layers with tie layer)</i>	Recyclable (≤ 90%) ** <i>(no Compatibilizer)</i>	Recycling compatible <i>(“PA 6 layers with tie layer”) *</i>
	Valuable material <i>(PA 6 layers with tie layer and Compatibilizer)</i>	Fully Recyclable (≤ 100%) ** <i>(Structure with Compatibilizer)</i>	

* Application started for the next Minimum Standard 2021; final wording not yet agreed

** Structure without printing inks or other components that affect recyclability

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First official certificates received.....

CERTIFICATE

Recycling Compatibility of Packaging Material

BASF SE
 Carl-Bosch-Strasse 38
 D-67056 Ludwigshafen am Rhein, Germany

The company receives the certification of recycling compatibility for the following plastic material.

Designation

Polyamide 6 (PA6)
 as layer in coextruded PE films, based on LDPE and/or LLDPE;
 in combination with ≥ 0.5 g per g PA of maleic anhydride-grafted PE as tie layer specified for PA/PE
 tested with $\leq 5\%$ by weight of PA6 in a PCR LDPE recyclate

Test result

Assessment via path/specification: Path 1: Plastic films / LDPE

Recyclate (final product): LDPE Regranulate

Test standard / scope of application:
 Requirements and assessment catalogue of the Institute cyclos-HTP for EU-wide certification (state: 07.10.2019) /
 Scope of validity according to nation states, see chapter 1
 DIN EN 13430 with regard to material recyclability in the post-use phase; also integrated
 The following reference processes, materials and applications are taken into consideration within the certification process:
 • Detection as feasible PE packaging in state-of-the-art sorting plants
 • Recyclate use for injection moulding and blown film applications
 • Test program based on CHI test protocol CHI-C8-PEF-12.0 with the use of PCR-based LDPE recyclate as reference

According to the CHI standard the plastic material is no contaminant in the tested application and in the above-mentioned material combination and can be considered as:

Recycling Compatible for PE Film Recycling
 (AT, DE, ES, FR, IT, NL, NO)

This certificate (No. 2187-2021-002124) is valid until the **31.05.2022** (1 year upon issue) relating to the countries identified in the assessment report. This certificate will lose validity in case of qualitative or quantitative changes of packaging components.

Aachen, dated 17.05.2021

Dr. Joachim Christiani
 Publicly appointed and sworn expert for the IHK for packaging waste recycling
 Competent authority: IHK Aachen

Dr. Roland Bothor
 Technical supervisor of the Investigations

Institute cyclos - HTP
 Institute cyclos-HTP GmbH
 Maria-Theresia-Allee 35 - 52064 Aachen
 phone: +49 (0) 241 / 949 00 - 0
 fax: +49 (0) 241 / 949 00 - 49

CERTIFICATE

Recyclability of a Packaging Material Group

BASF SE
 Carl-Bosch-Strasse 38
 D-67056 Ludwigshafen am Rhein, Germany

The company receives the certification of recyclability for the following packaging materials.

Designation

LDPE-based multilayer packaging films with Polyamide 6 (PA6) including $\leq 30\%$ by weight of PA6;
 in coextruded polyethylene films, based on LDPE and/or LLDPE; packaging size $\geq A5$;
 with ≥ 0.5 g per g PA of maleic anhydride-grafted PE as tie layer specified for PA/PE;
 not including printing inks, adhesives or other components that can affect the recyclability

Test result

Assessment via path/specification: Path 1: Plastic films / LDPE

Recyclate (final product): LDPE Regranulate

Test standard / scope of application:
 Requirements and assessment catalogue of the Institute cyclos-HTP for EU-wide certification (state: 07.10.2019) /
 Scope of validity according to nation states, see chapter 1
 DIN EN 13430 with regard to material recyclability in the post-use phase; also integrated
 The following reference processes, materials and applications are taken into consideration within the certification process:
 • Detection as feasible PE packaging in state-of-the-art sorting plants
 • Recyclate use for injection moulding and blown film applications
 • Test program based on CHI test protocol CHI-C8-PEF-12.0 with the use of PCR-based LDPE recyclate as reference

According to the CHI standard the recyclability of the packaging component amounts to:

$\geq 70\%$ (AT, DE, ES, FR, IT, NL, NO)

This certificate (No. 2187-2021-002126) is valid until the **31.05.2022** (1 year upon issue) relating to the countries identified in the assessment report. This certificate will lose validity in case of qualitative or quantitative changes of packaging components.

Aachen, dated 17.05.2021

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 with ≥ 0.5 g per g PA of maleic anhydride-grafted PE as tie layer specified for PA/PE;
 with ≥ 0.15 g per g PA of Dow Fusabond E226 or chemically comparable compatibilizer in a neighbouring PE layer of the structure; not including printing inks, adhesives or other components that can affect the recyclability

Test result

Assessment via path/specification: Path 1: Plastic films / LDPE

Recyclate (final product): LDPE Regranulate

Test standard / scope of application:
 Requirements and assessment catalogue of the Institute cyclos-HTP for EU-wide certification (state: 07.10.2019) /
 Scope of validity according to nation states, see chapter 1
 DIN EN 13430 with regard to material recyclability in the post-use phase; also integrated
 The following reference processes, materials and applications are taken into consideration within the certification process:
 • Detection as feasible PE packaging in state-of-the-art sorting plants
 • Recyclate use for injection moulding and blown film applications
 • Test program based on CHI test protocol CHI-C8-PEF-12.0 with the use of PCR-based LDPE recyclate as reference

According to the CHI standard the recyclability of the packaging component amounts to:

100% (AT, DE, ES, FR, IT, NL, NO)

This certificate (No. 2187-2021-002126) is valid until the **31.05.2022** (1 year upon issue) relating to the countries identified in the assessment report. This certificate will lose validity in case of qualitative or quantitative changes of packaging components.

Aachen, dated 17.05.2021

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 Competent authority: IHK Aachen

Dr. Roland Bothor
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.....more will follow

BASF und Cyclos-HTP untersuchen mechanische Recyclingfähigkeit von PA/PE-Verbundfolien

Nach verschiedenen BASF-internen Studien bestätigt nun auch eine kürzlich abgeschlossene Untersuchung von cyclos-HTP die Recyclingverträglichkeit von PE/PA6-Verbundfolien im Polyethylenfolienstrom aus Haushaltsverpackungsabfällen. Entgegen der verbreiteten Meinung, dass PE/PA-Verbunde nicht mechanisch recycelt werden können, kommt die von BASF beauftragte Studie nach Anwendung der Testprotokolle von cyclos-HTP zu der Erkenntnis, dass PA6-Barrierschichten mit Haftvermittlern in coextrudierten Verbundfolien in Bezug auf das mechanische Recycling von LDPE-Folien nicht nur gut verträglich sind, sondern sogar das Eigenschaftsniveau von industriellen Polyethylenrezyklaten positiv beeinflussen. Weitere Untersuchungen mit PE/CoPA, PE/CoPA/EVOH sowie PA-haltigen Kaschierverbundstrukturen wurden begonnen. Im nächsten Schritt sind nun mechanische Recyclingversuche im Industriemaßstab geplant. Eine Anpassung des Mindeststandards zur Bemessung der Recyclingfähigkeit sowie weiterer Design-for-Recycling-Leitlinien wird angestrebt. Die detaillierten Untersuchungsergebnisse wurden am 18. März in einem Webinar von BASF vorgestellt. Die Aufzeichnung des Webinars und die gezeigte Präsentation finden Sie hier: https://packaging-print.basf.com/global/en/interpack-2021/Mechanical_recycling_of_polyamides_in_multilayer_film_structures.html

Es ist an der Zeit, die Kategorisierung von Polyamid 6 und auch der verwandten PA6/6.6 Co-Polyamide als ‚unverträgliche‘ Kontaminanten, zu korrigieren und auf eine solide aktualisierte Basis zu stellen.

Dr. Rolf-Egbert Grützner
Senior Manager Technical Support
für die Ultramid® Extrusionspolyamide

KUNSTSTOFFWEB NACHRICHTEN TECHNOLOGIE
BASF: MEHRSCHICHTFOLIEN MIT PA 6 SIND RECYCLINGFÄHIG

BASF: Mehrschichtfolien mit PA 6 sind recyclingfähig

02.07.2021

Das Institut cyclos-HTP GmbH, Aachen, hat die von der BASF, Ludwigshafen, beauftragten Untersuchungen zur Neubewertung der Recyclingfähigkeit von PA 6 in coextrudierten PE/PA6-Mehrschichtverbundfolien im haushaltsnahen Verpackungsabfall abgeschlossen. Das zentrale Ergebnis: Mehrschichtfolien auf Basis PE/PA 6 wird eine Recyclingverträglichkeit für den PE-Folienstrom attestiert. Dies wurde für PA-6-Anteile von bis zu 30 % in den ursprünglichen Folien untersucht.

Dieses Ergebnis soll die Grundlage für eine Überprüfung der Einstufung von PA 6 im „Mindeststandard für die Bemessung der Recyclingfähigkeit von systembeteiligungspflichtigen Verpackungen gemäß § 21 Abs. 3 VerpackG (Verpackungsgesetz)“ der Stiftung Zentrale Stelle Verpackungsregister bilden. PA 6 wird im Mindeststandard im Anhang 3 bisher als „unverträgliche“ Komponente, beispielsweise im Abfallstrom der Verpackungsgruppe „Folie und PE-LD“ aufgeführt. „Wir freuen uns, dass durch cyclos-HTP eine wissenschaftlich fundierte Grundlage zur Neubewertung erarbeitet werden konnte. Es ist an der Zeit, die Kategorisierung von Polyamid



We create chemistry