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

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partially a joint project of



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Why is the topic that important?

- **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

⁽³⁾ Illing, G.: Makromolekulare Mehrstoffsysteme. Schlagfeste PA-PO-Legierungen, ein Beitrag zur Strukturaufklärung; Die Angew. Makrom. Chemie 95, 1 (83-108) 1981

⁽⁴⁾ DE19502819 “Tough PA 6 moulding composition produced from entirely recycled materials”; Grützner, R.E.; Koine, A. (1996)

⁽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(blow)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(blow)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

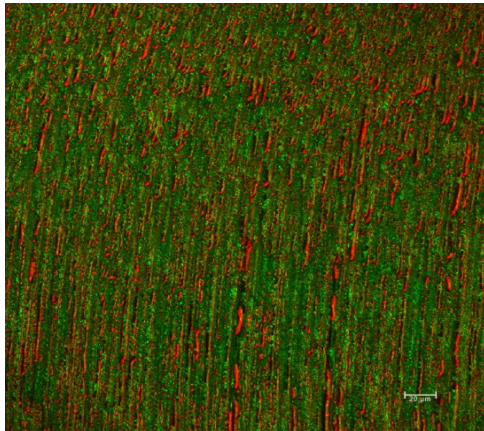
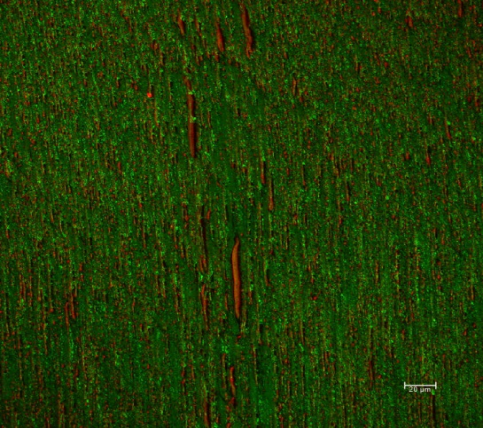


S Gran 95, NGR Recycling Machines, Austria

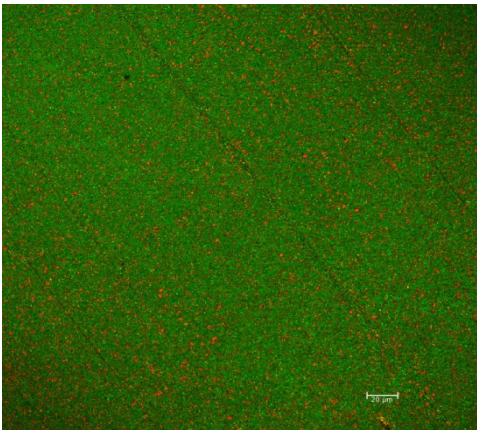
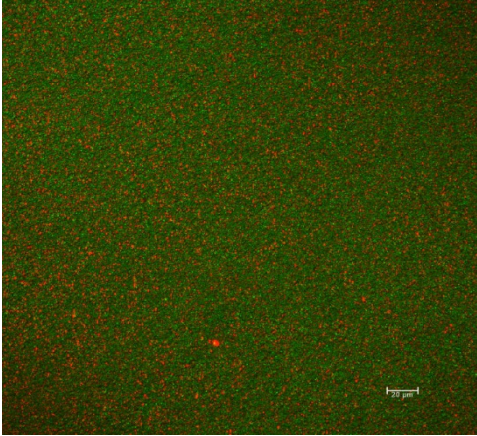
Combination of shredder/feeding unit with single screw extrusion device, up to 400 kg/h throughput, 210 - 240°C melt temperature, no additional drying step of regranulates

Morphologies of regranulate pellets made from PE/PA6 film waste

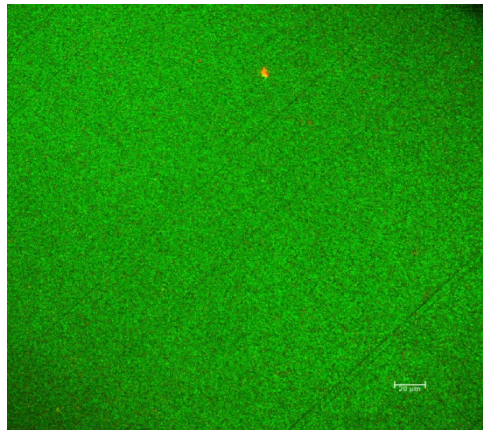
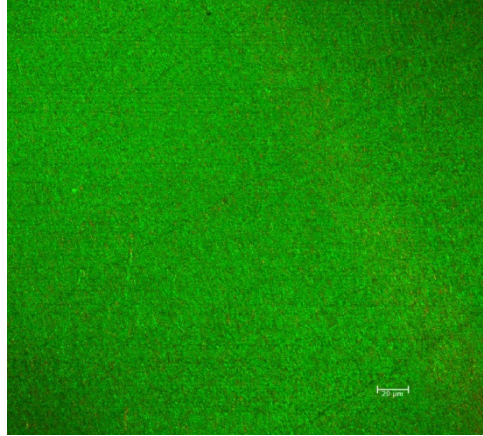
Reg A



Reg R



Reg F



Compatibilizers in original film structures already generates well homogenized PE/PA6 – regranulates!

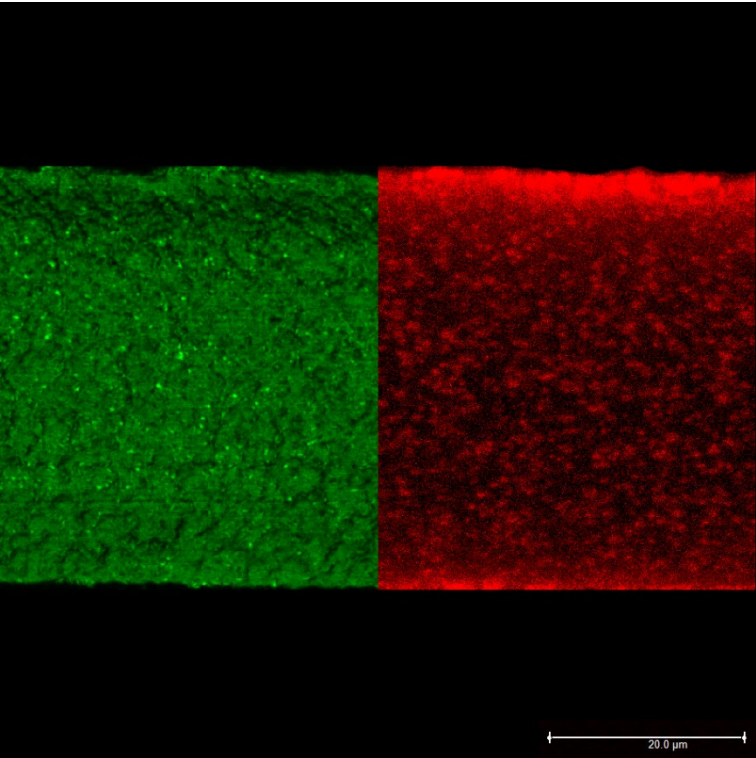
examples here = 80%PE/20%PA6 without (A) and with compatibilizers (R,F)

Recipe overview I – Focus (Pre) - Compatibilization

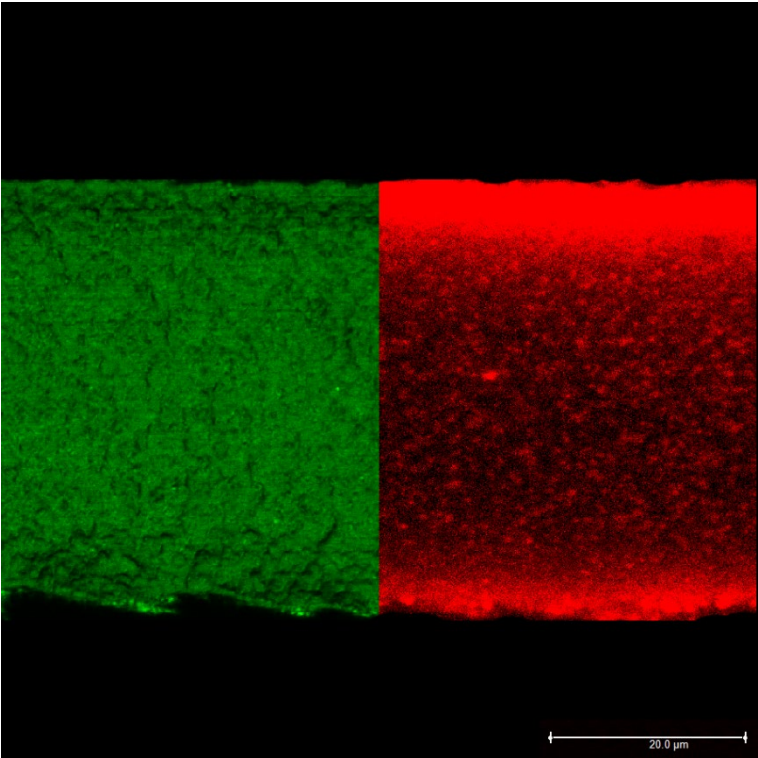
Trials	Reg A (%/%PA)	Reg R (%/%PA)	Reg F (%/%PA)	PE Regranulate (%)	Compatibiliser F* (%)
1.0	-	-	-	100	-
1.1	100 / 20	-	-	-	-
1.2	-	100 / 20	-	-	-
1.3	-	-	100 / 20	-	-
1.4	95 / 19	-	-	-	5
1.5	-	95 / 19	-	-	5
1.6	-	-	95 / 19	-	5
1.7	40 / 8	-	-	60	-
1.8	-	40 / 8	-	60	-
1.9	-	-	40 / 8	60	-
1.10	50 / 10	-	-	47	3
1.11	-	50 / 10	-	47	3
1.12	-	-	50 / 10	47	3

* Fusabond E226, all components mixed as salt & pepper blends prior to blown film process directly!

Morphologies I – Monolayer blown films I

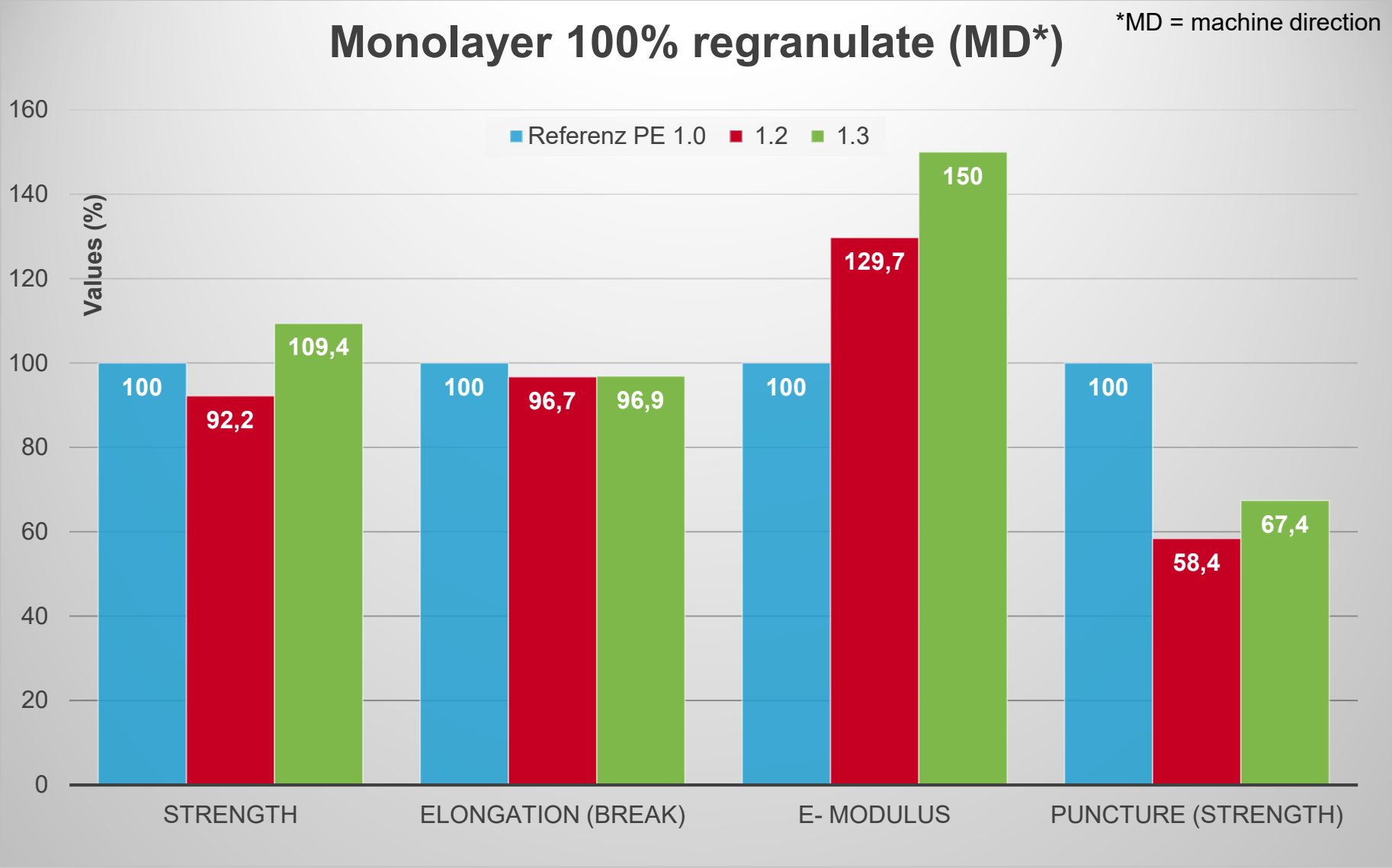


PE/PA6 Blend 1.2 (pre-compatibilized Reg R)



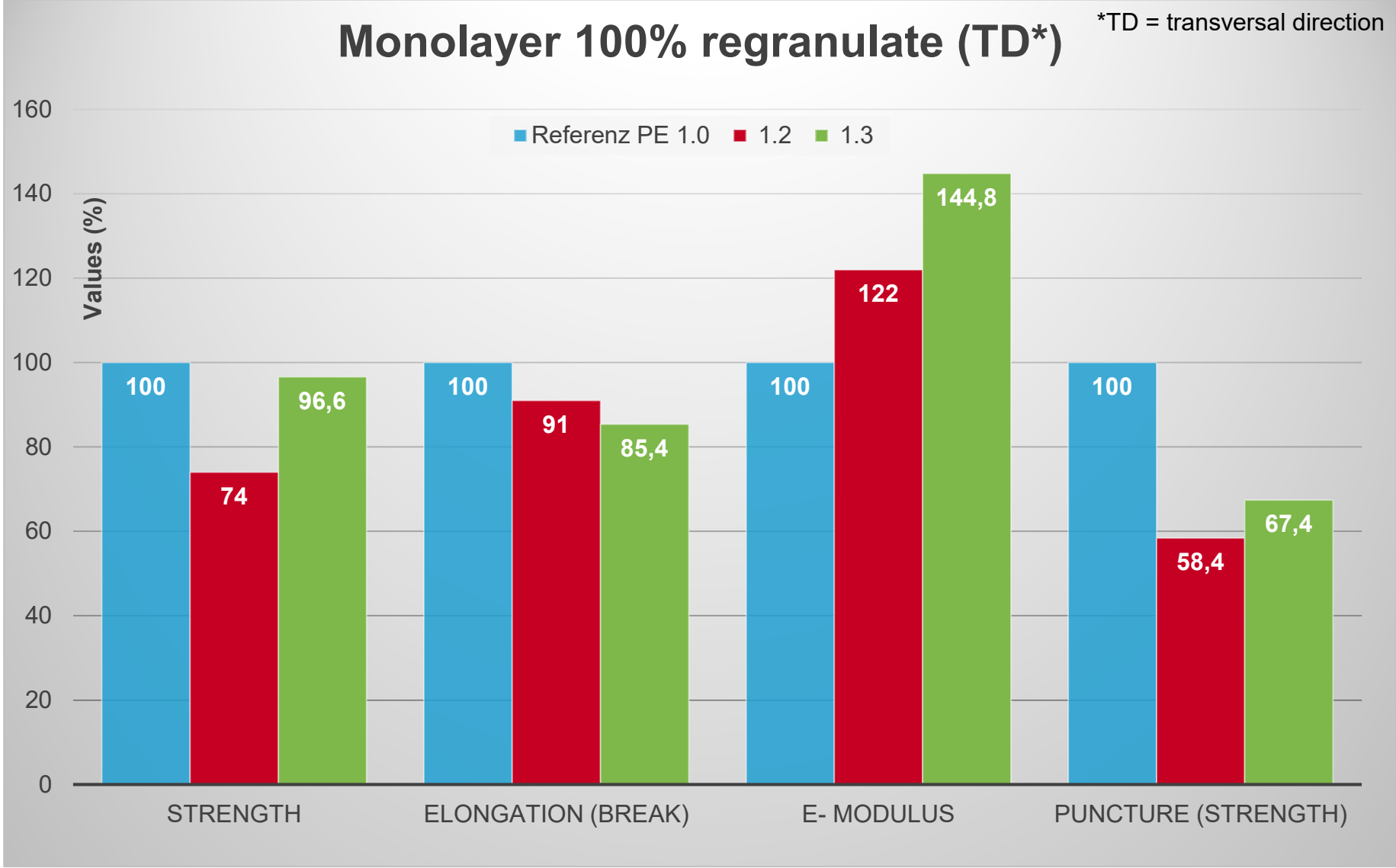
PE/PA6 Blend 1.3 (pre-compatibilized Reg F)

Mechanical properties in comparison Ia (3 Basic recipes)



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 Ib (3 Basic recipes)



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

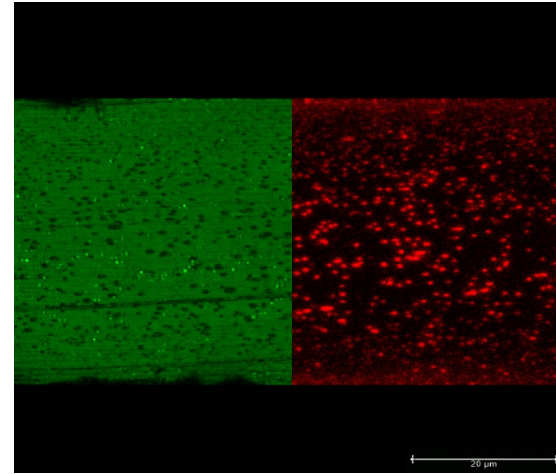
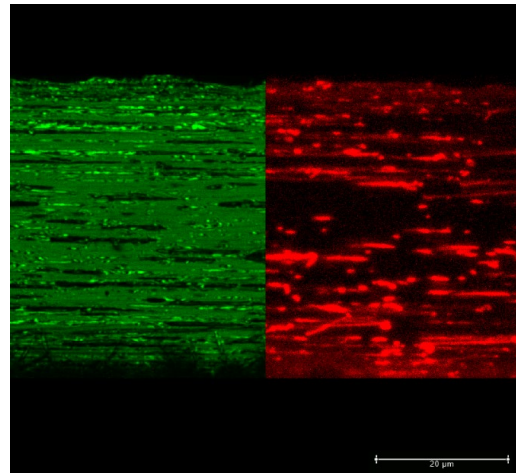
Trials	Reg A* (%/ %PA)	PE Regranulate (%)	Compatibilizer F** (%)
1.0	-	100	-
1.1	100 / 20	-	-
3.1	50 / 10	50	-
3.2	37,5 / 7,5	62,5	-
3.2	25 / 5	75	-
1.4	95 / 19	-	5
4.2	50 / 10	45	5
1.10	50 / 10	47	3
4.3	37,5 / 7,5	57,5	5
4.4	25 / 5	70	5

* 20% B40LN
 ** Fusabond E226

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

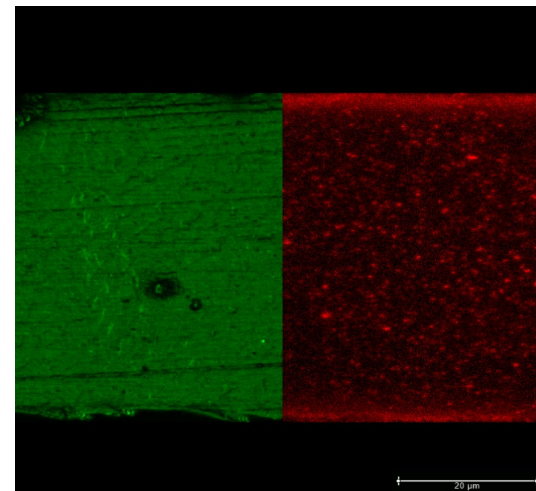
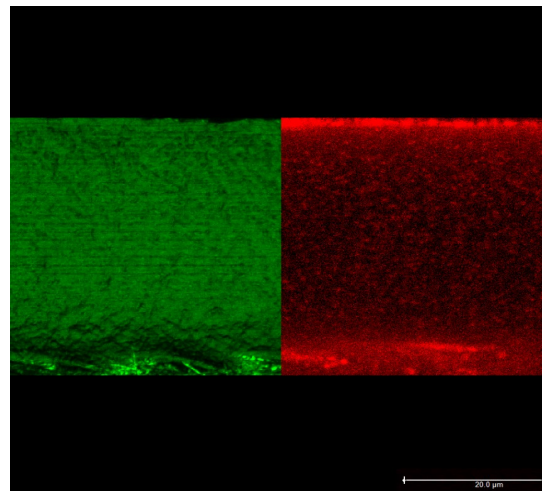
- Weber 30 aircooled blown film line
- 30mm screw, L/D = 25
- Die diameter 50mm
- Lay flat 350 mm,
- Temperatures 235°C/240°C

Morphologies II – Monolayer blown films II (Dilution trials, excerpts)



Monolayer 3.2 = 7,5% B40LN Monolayer 3.3 = 5% B40LN

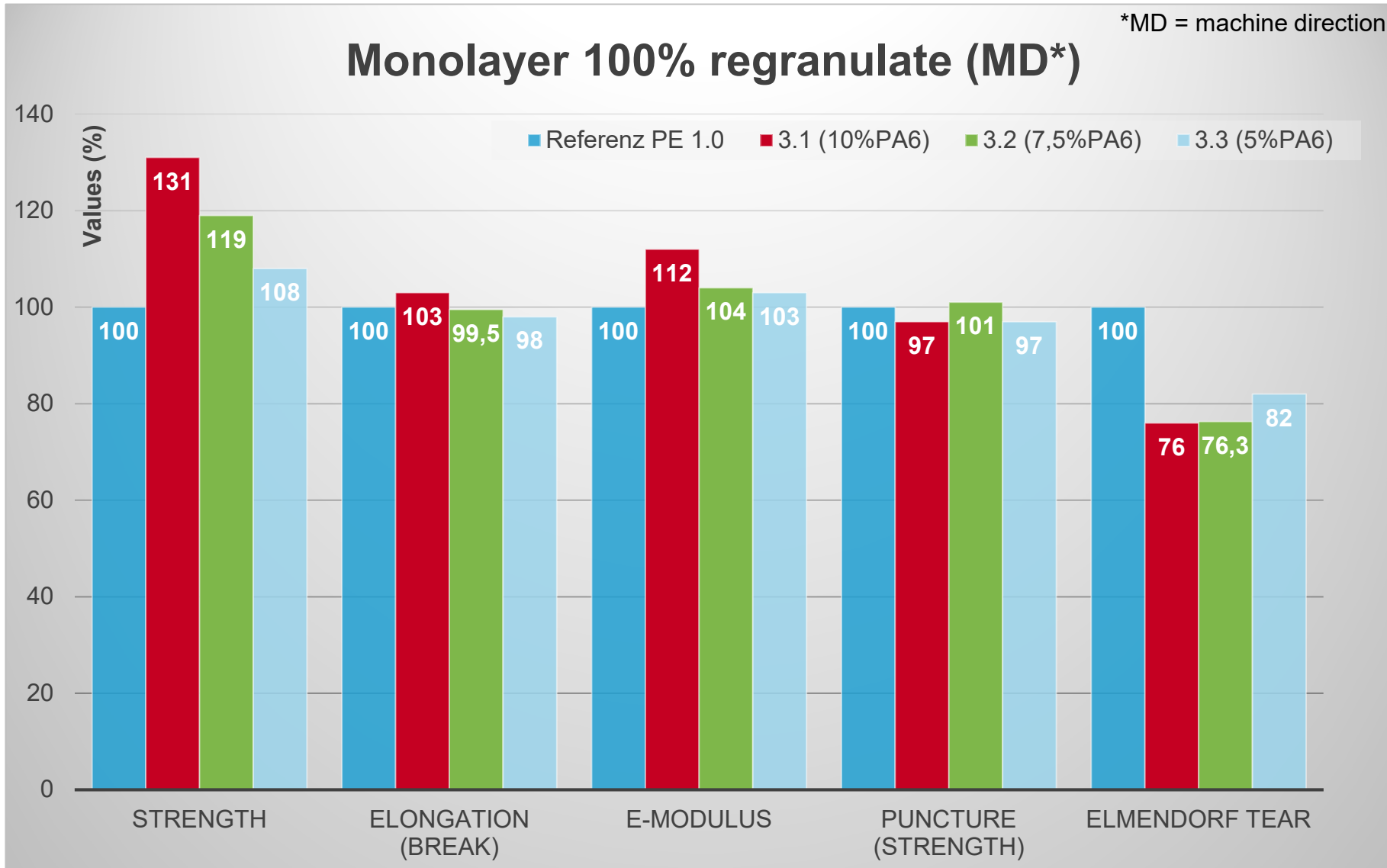
without compatibilizer



Monolayer 1.4* = 19% B40LN Monolayer 4.2* = 10% B40LN

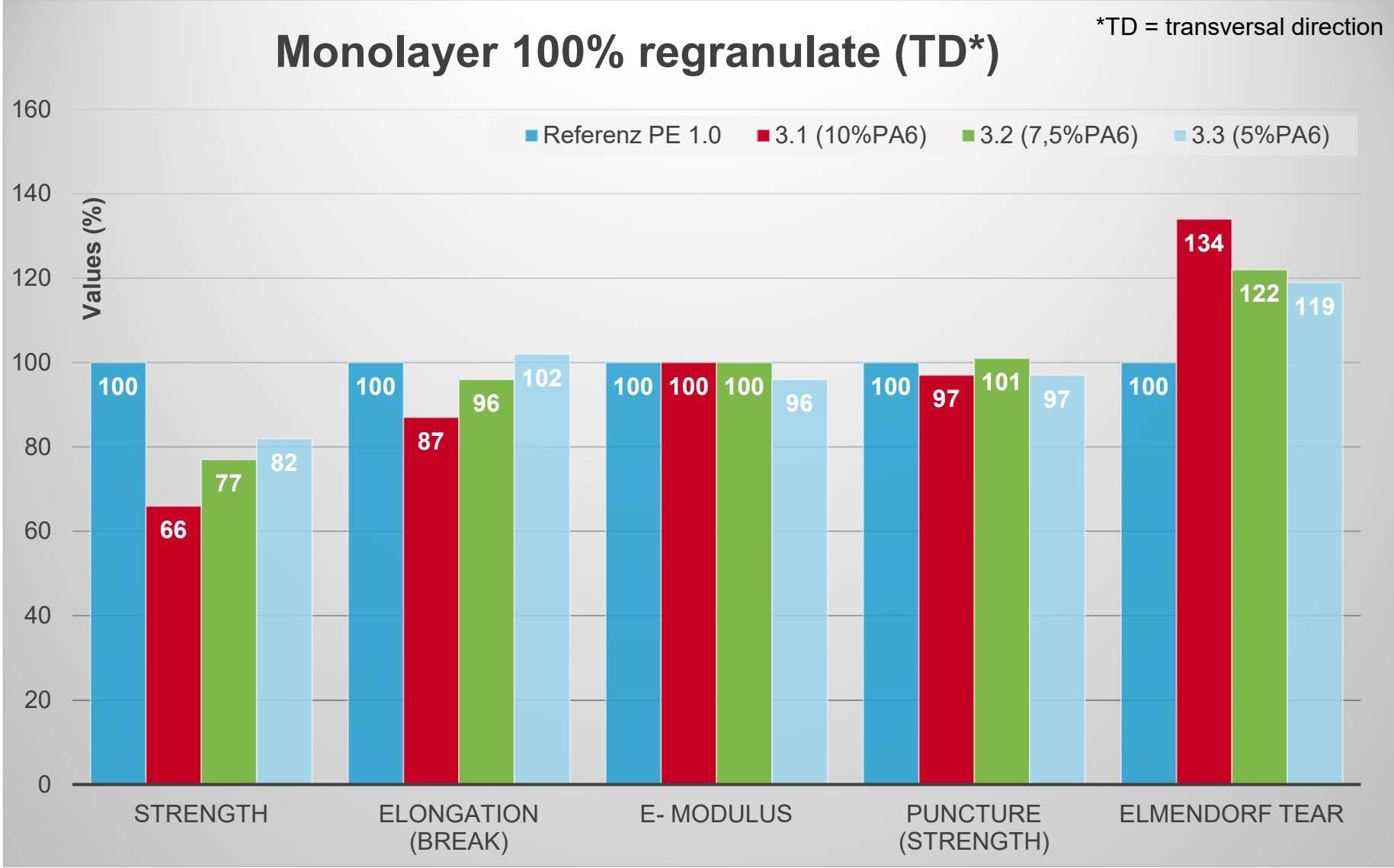
* 5% Fusabond E226

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



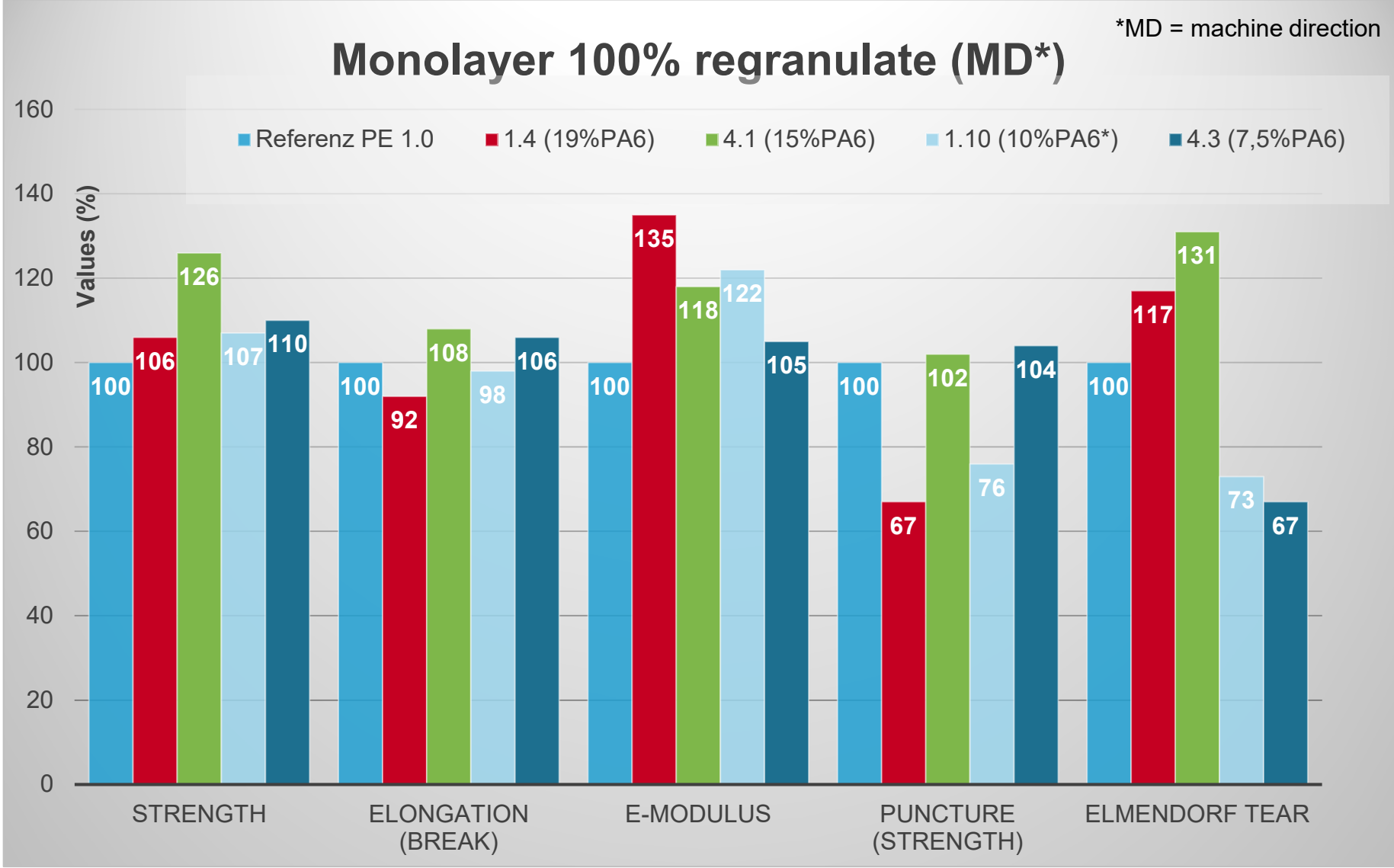
All components mixed as salt & pepper blends prior to blown film process directly!

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



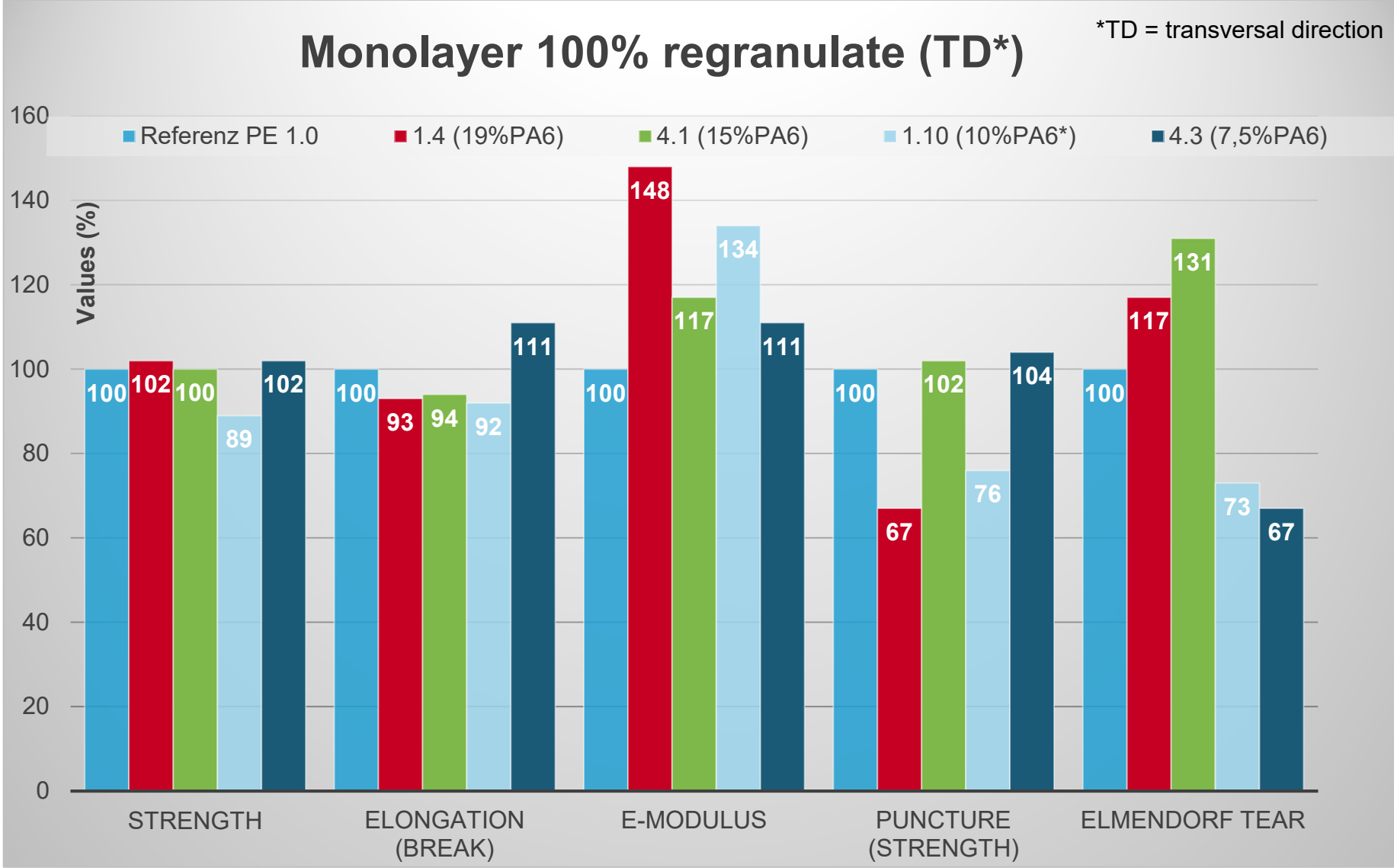
All components mixed as salt & pepper blends prior to blown film process directly!

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)



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:
- All other trials:

PE(12,5µm)/PE(45µm)/PE(12,5µm)
 PE(12,5µm)/PE + Regranulat(45µm)/PE(12,5µm)

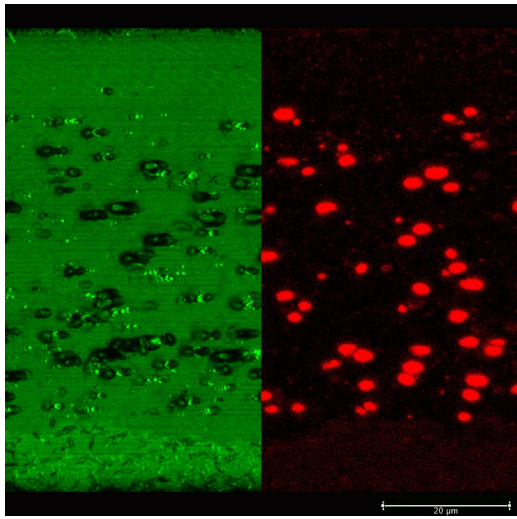


Trials	PA 6 (B40LN*, %)	Reg A (%)	Reg A** (%)	Reg R (%)	Reg F (%)	PE (%)***	Comp.R**** (%)
2	6,4# (4##)	-	-	-	-	93,6	-
4b	6,4# (4##)	-	-	-	-	92,0	1,6
6b	-	-	78# (10##)	-	-	20,0	2,0
6c	-	-	98# (12,5##)	-	-	-	2,0
18b	-	32# (4##)	-	-	-	68,0	-
20	-	-	-	32# (4##)	-	68,0	-
22	-	-	-	-	32# (4##)	68,0	-

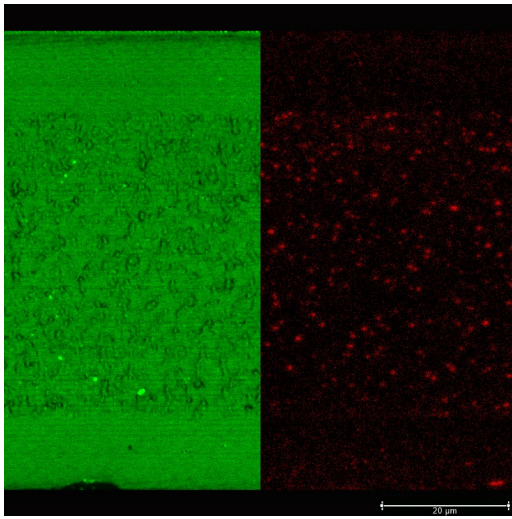
- Varex II 3 – layer aircooled blown film line
 - lay flat 1700 mm,
 - melt temperature of 250°C in core layer
 - 400 kg/h throughput

- * 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**

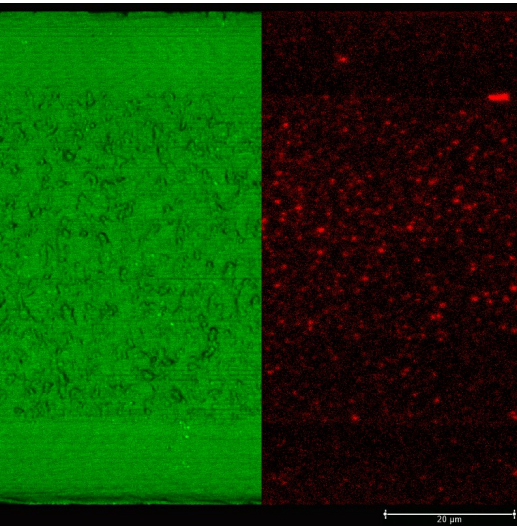
Morphologies III – Multilayer films with PE/PA6 regranulate content



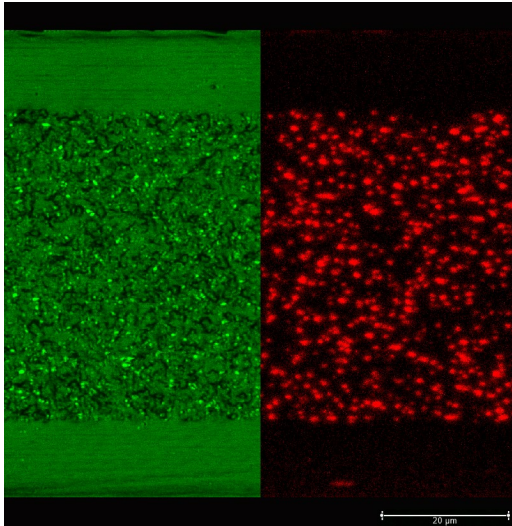
Multilayer 18b = 6,4% PA 6 in core



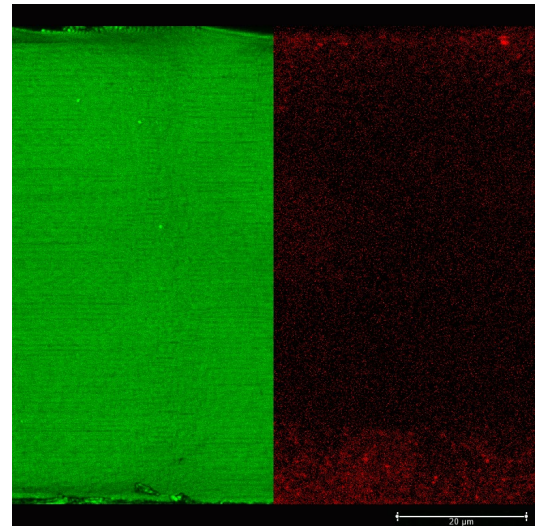
Multilayer 22 = 6,4% PA in core, 1,6 %F



Multilayer 6b = 15,6% PA 6 in core, 2%R

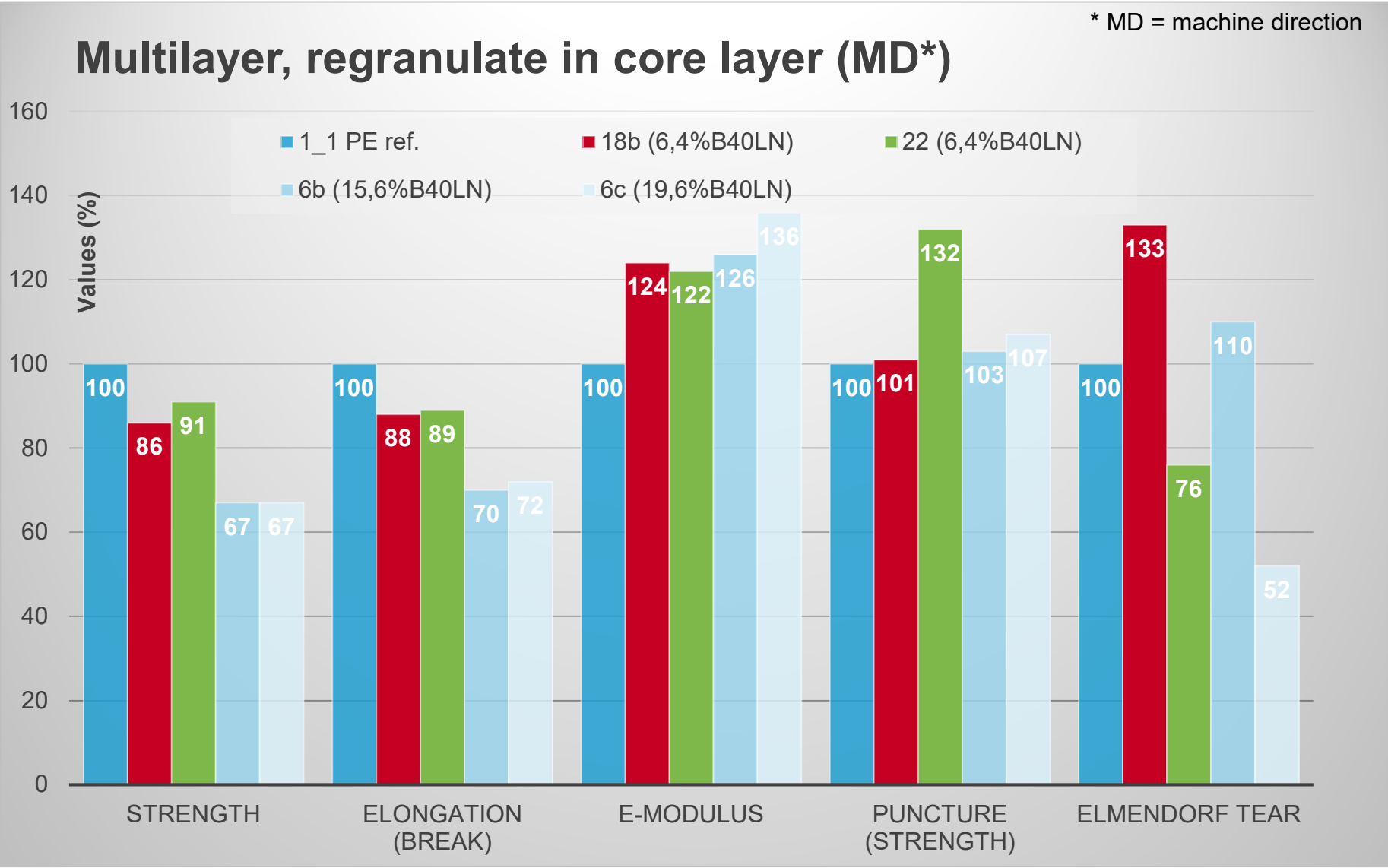


Multilayer 6c = 19,6% PA 6 in core, 2%R

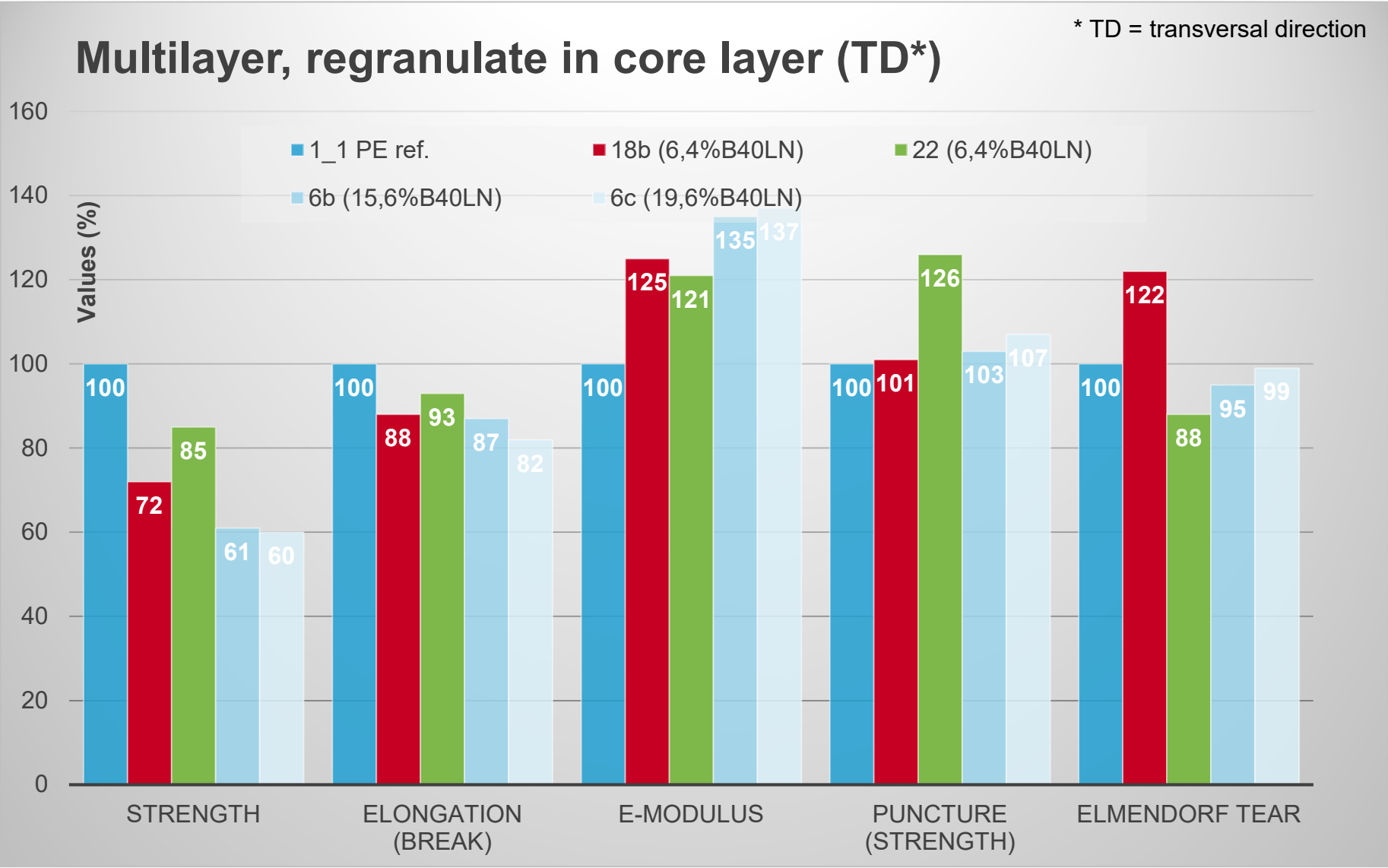


Multilayer 1_1 = PE Reference

Mechanical properties in comparison IVa - Multilayer films (Excerpts)



Mechanical properties in comparison IVb - Multilayer films (Excerpts)



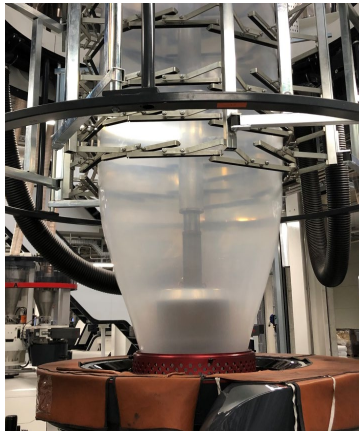
Virgin blend

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

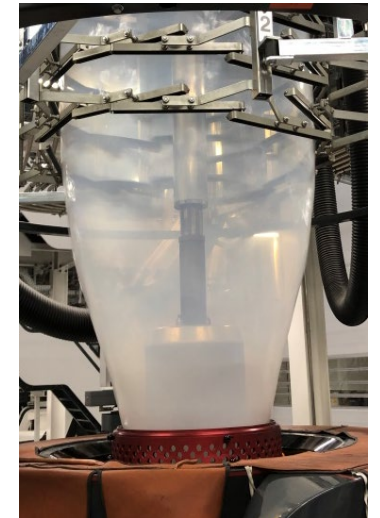
Secondary Film Basic trial

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

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



- Very bad optic due to strong inhomogeneities



- 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%)



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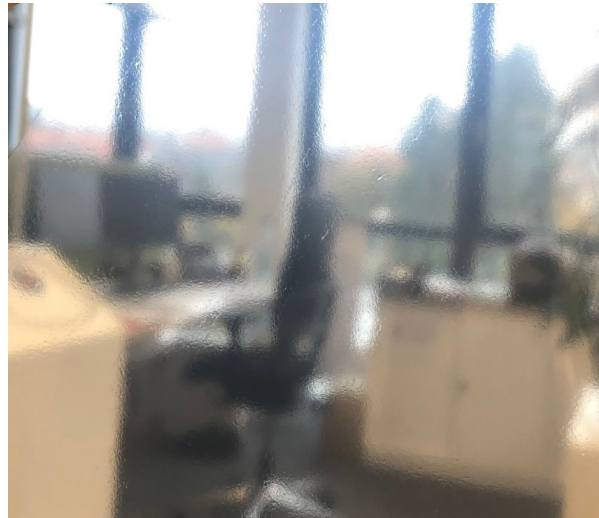
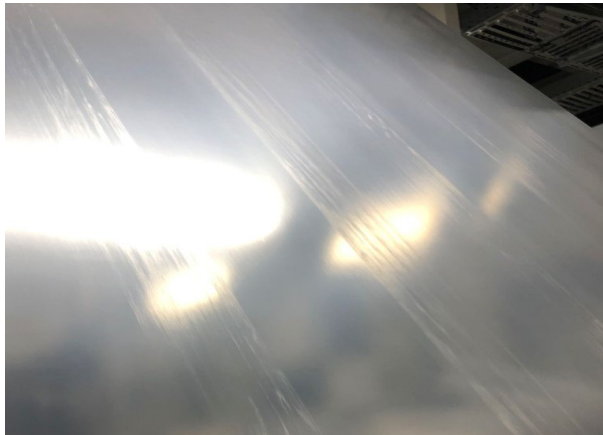
PE/PA6 – regranulates in core layer

Secondary Film

Dosing of PE/PA6 - regranulates to PE (with & without compatibilizer)

70% 5056G	48% GM8090	70% 5056G
30% 310E	20% 310E	30% 310E
	32% BASF_Regr. A	

70% 5056G	48% GM8090	70% 5056G
30% 310E	20% 310E	30% 310E
	32% BASF_B / NGR_2	



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

- Good film optics & quality
- No spiral flow marks / lines
- No difference (subjective) between industrial (BASF) and tech center (NGR) regranulates



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PE/PA6 – regranulates in core layer

Secondary Film

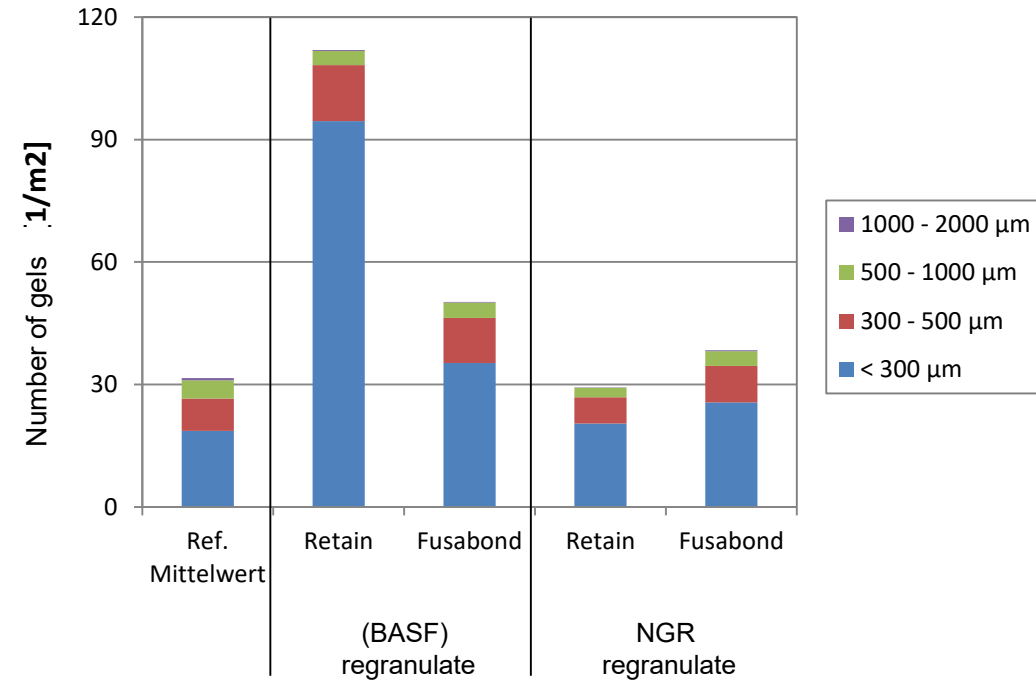
Dosing of PE/PA6 – regranulates to PE (pre-compatible recipes)

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

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

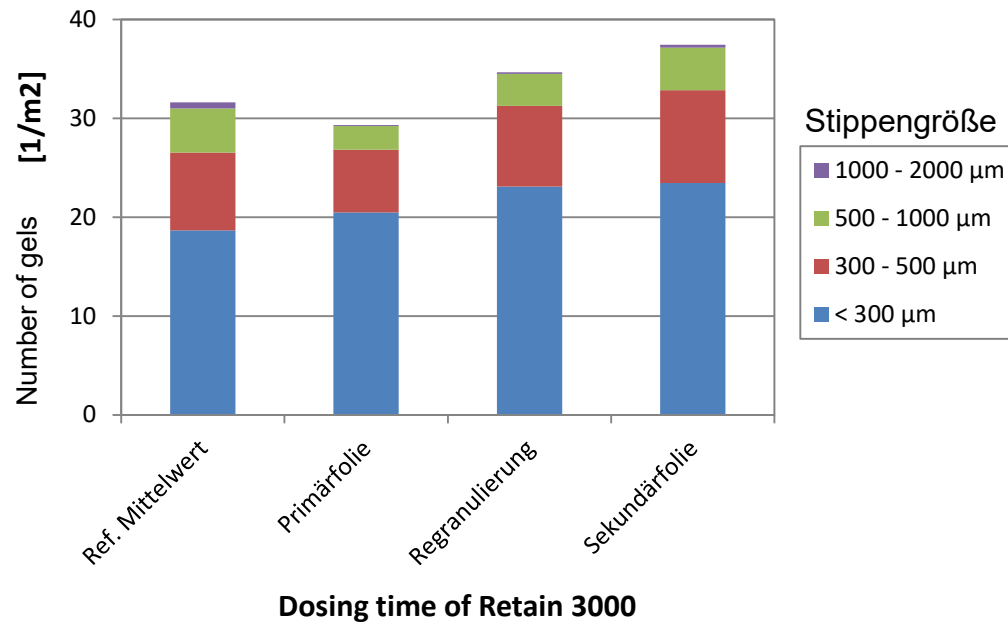
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PE/PA6 – regranulates in core layer

Secondary Film

Influence of dosing location (time) of compatibilizer

70% 5056G 30% 310E	48% GM8090 20% 310E 32 % Regranulate + Retain 3000	70% 5056G 30% 310E
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- 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.



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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 \geq 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 processable 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 Recyclclass 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.



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