Giving a second life to plastics
How to restore polymer performances?

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Within plastic waste management material recycling is gaining increased attention. The low public opinion about the value of plastics particularly in packaging leads to new legislations around the globe. Many of these new regulations are setting goals for the recycling quote. In some applications (e.g. PET bottles), the material recycling is well established. Other applications (e.g. films, …) are still underdeveloped regarding mechanical recycling, partially due to lack of commercial incentives and missing appropriate separation techniques. However, to provide incentive for using post used plastics it is important that recyclates can be used in higher added value applications.

The plastic compound for a specific application is typically designed to meet the requirements for processing and one life cycle. No surprise that stabilizer residues from the 1st life and rheological properties of the recyclate are hardly appropriate for a higher added value in a 2nd or 3rd life.

Consequently, post used recyclate needs to be upgraded.

Post-consumer recyclate (PCR) materials are influenced by the multiple streams and qualities, resulting from the collection, sorting and extrusion processes used. There are various influencing factors that determine the quality of a recyclate, one important being the composition.

Understanding the effect of the contamination of a polyethylene stream by even a small amount of polypropylene is important for upgrading such a material. This is illustrated in the figure 1 below with mixtures of post used HDPE and PP bottle scrap. 100% virgin HDPE bottle grade material is given as a reference. The 95% HDPE/5% PP recyclate mixture shows a significantly reduced thermal stability compared to 100% virgin HDPE, from more than 120 days down to roughly 20 days. With restabilization, the long-term thermal stability can be corrected. Increasing concentration of PP “contaminant” makes restabilization more demanding, but still possible. Other contaminants such as PVC are even more detrimental at much lower concentrations (PVC). This emphasis the role of the collection and sorting process for the quality of recyclates.

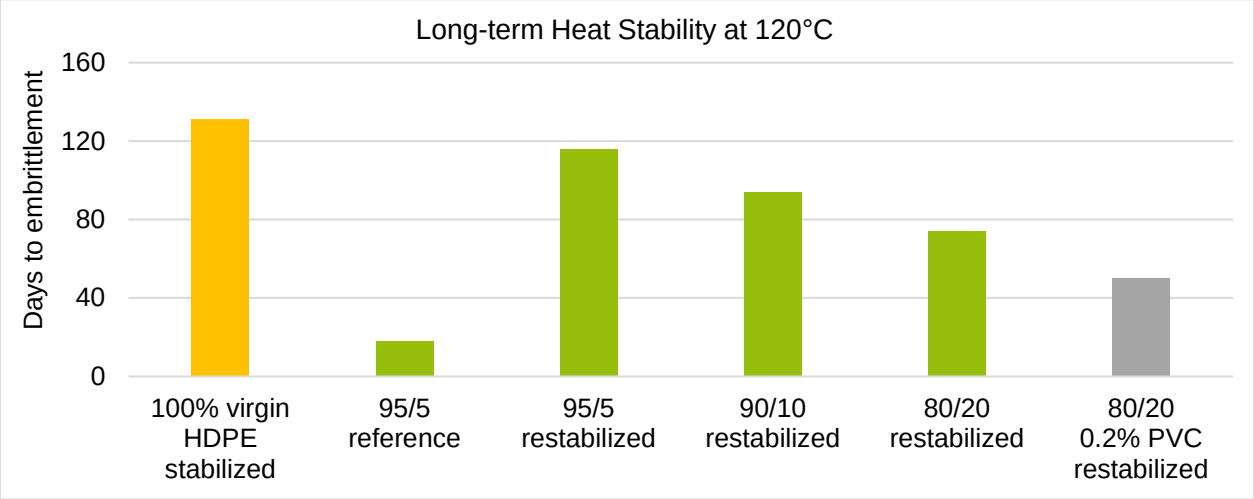

Fig. 1 – Influence of PP contamination on the thermal stability of HDPE - Extrusion twin screw and injection molding at max. 240°C, 2mm plaques

Another example for the effect of the contamination is to look at the influence of polypropylene on the properties of polyethylene films. Many packaging films are based on L-LDPE and LDPE or combinations of those. Therefore, a PCR resulting from the collection of packing films is very likely a mixture of them, possibly contaminated by PP film.

The influence of polymer composition in multiple single-screw extrusion is illustrated in figure 2. Here virgin polymers were used for the purpose to eliminate the effect of other impurities.

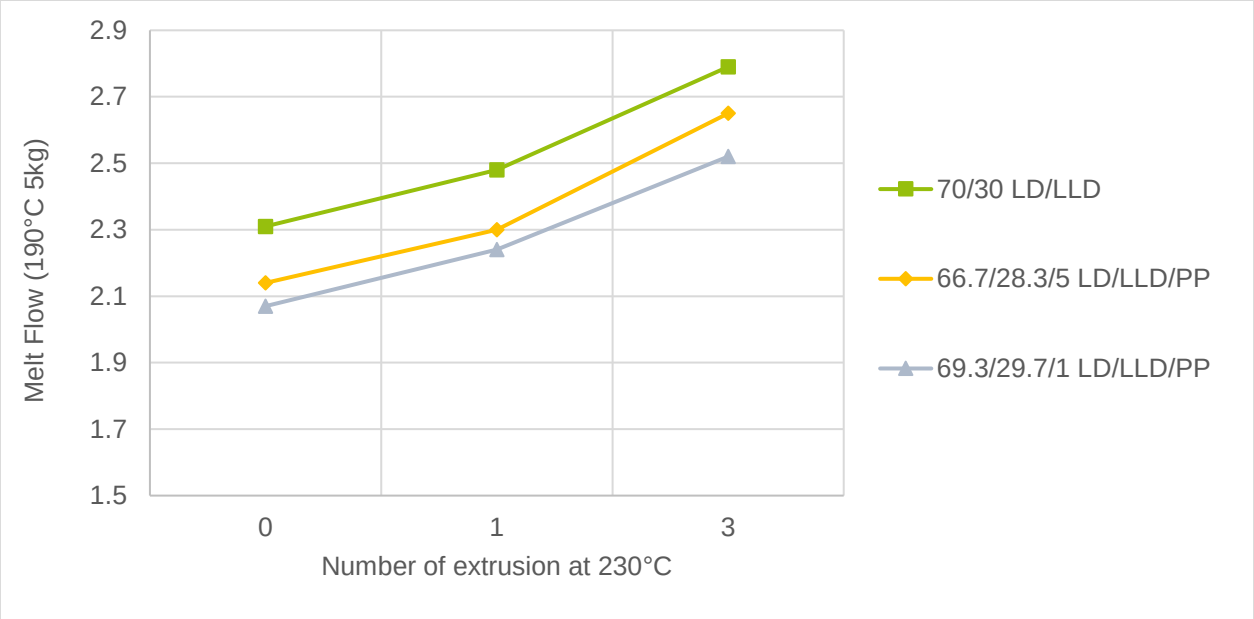

Fig. 2 Influence of polymer composition on processing at 230°C

The addition of 1% PP to the 70:30 LDPE/LLDPE mixture reduced the melt flow. This effect seems to be depending on the PP concentration.

The same blends were used in blown film experiment and the tensile properties of the films were tested. The results are summarized in figure 3 and 4.

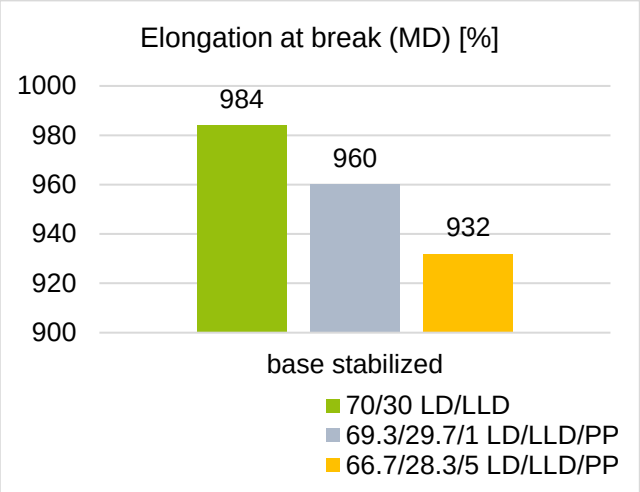

Fig. 3: Elongation at break of 100µm blown film

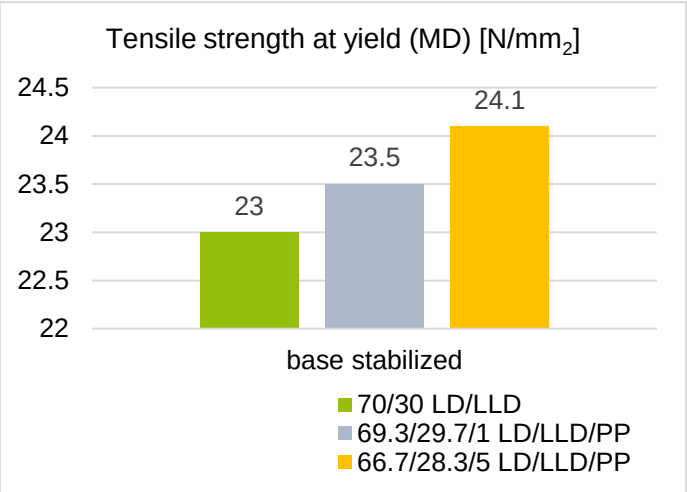

Fig. 4: Tensile strength at yield of 100µm blown film

The addition of 5% PP to the 70:30 PE mixture reduced the elongation significantly but improved the tensile strength at yield. It shows the potential and necessity to adapt the properties required for a final application.

As conclusions from this case study with virgin polyolefin film mixture, we found that even without impurities a varying polymer blend composition leads to fluctuating properties. Processing behavior, film properties and durability are not affected in the same way and the blend composition should be optimized to improve properties.

A second case study was done with two commercial polyolefin recyclates (source Switzerland). The purpose was to investigate ways to improve the quality of a given recyclate and to study the influence of the composition on processing and blown film properties

The first step was to analyse the recyclates for residual antioxidants and possible contaminants.

	Quality 1	**Quality 2**
		
color	grey	black
Irganox 1010	40 ppm	50 ppm
Irganox 1076	230 ppm	200 ppm
Irgafos 168	60 ppm	90 ppm

Irgafos 168-phosphate	460 ppm	510 ppm
UV absorber	10 ppm	50 ppm
Polymer mix	LD/LLD	LD/LLD
PP content	~1%	~1%
impurities	Na, Al, Zn, Cl, Ti, Fe, ~700 ppm	Cr, Cu, Na, Al, Cl, Ti, Fe, Mg ~2700 ppm

Analytical results show very little residual active processing stabilizer Irgafos 168 left (the majority was converted to the inactive Irgafos 168-phosphate) and a low level of phenolic antioxidants. Main differentiator is the amount of metal impurities (such as Cu, Fe), which are relevant when acids are available. Additionally, different odor levels were observed.

Multiple extrusion of the recyclates stabilized with two different systems are shown in Figure 5 and 6. Both qualities show quite some differences in response.

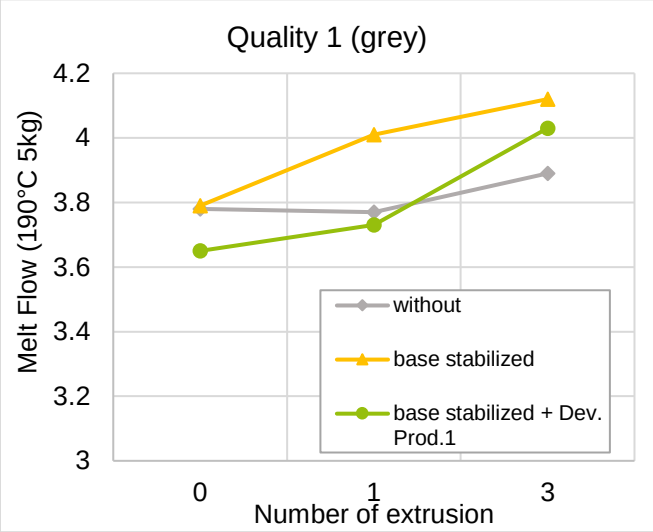

Fig. 5: Multiple pass extrusion at 230°C of grey recyclate

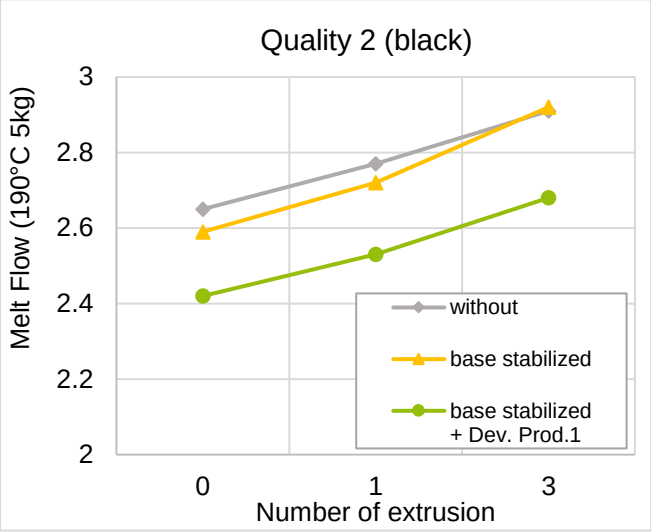

Fig.6: Multiple pass extrusion at 230°C of black recyclate

The same formulations were used in blown films experiment were the tensile properties of films were measured. The results are plotted in figures 7 and 8 below.

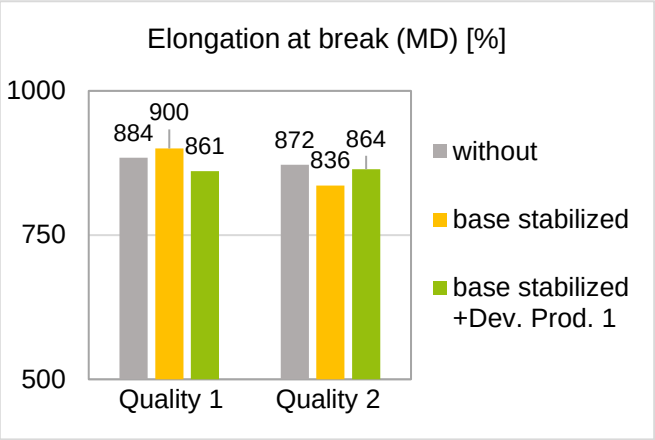

Fig. 7: Elongation at break of 100µm blown film

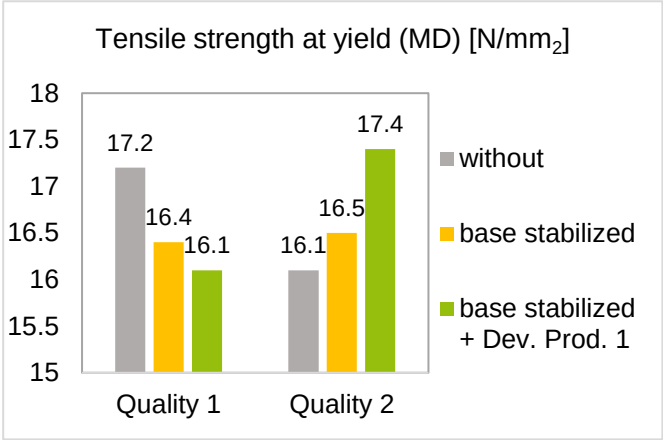

Fig. 8: Tensile strength at yield of 100µm blown film

The grey (quality 1) and black (quality 2) recyclates behave differently and need more tailored solutions. The effect of Developmental Product 1 on tensile strength is more pronounced with Quality 2 material. The additive package needs to be adjusted to Quality 1 and Quality 2. The results of Quality 1 are not in line with MFI measurement. However, Quality 2 fits well with some rheological measurements obtained on an extensional rheometer (figure 9). The melt strength increased with additivated solutions, correlating with increased bubble stability. The slope at low acceleration with modifier is steeper, indicating higher elongational viscosity. Further optimization is of course possible.

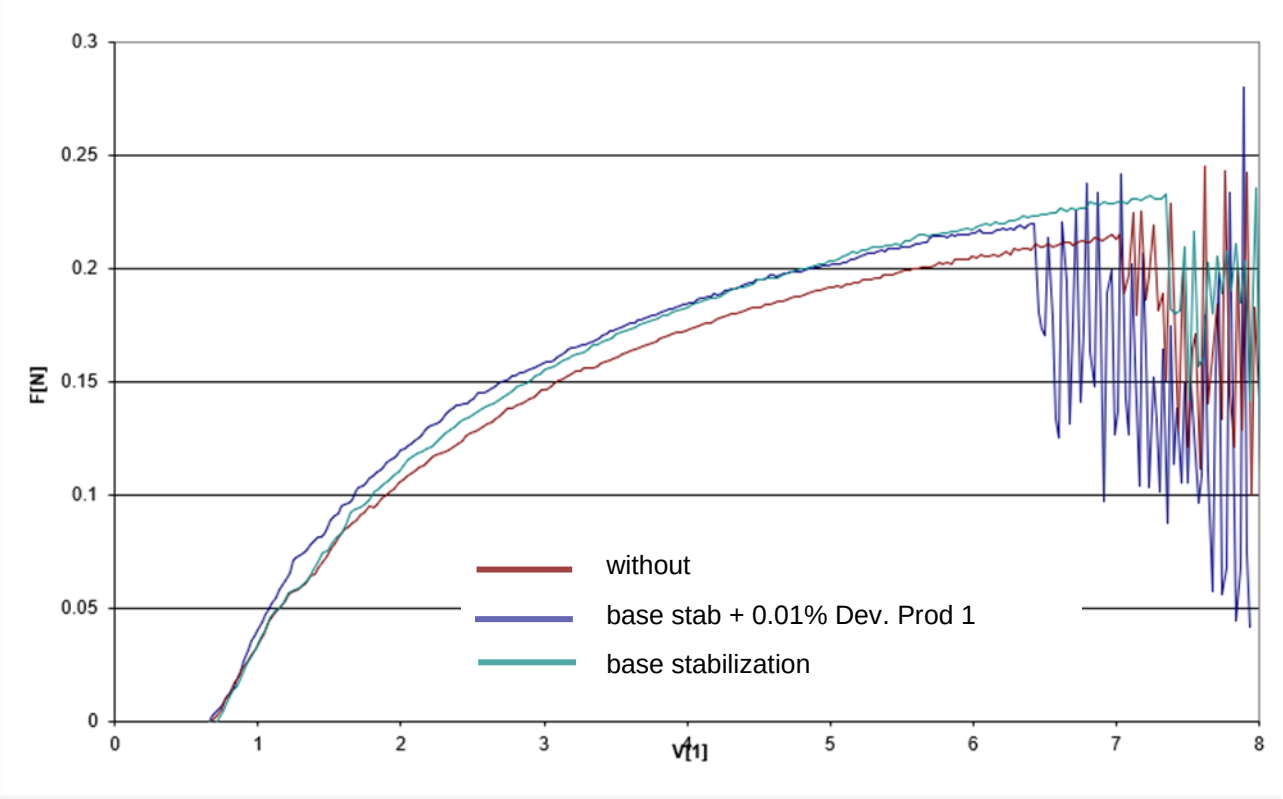

Fig. 9: Rheotens measurement at 190°C, acceleration: 2.4 mm/sec of black recyclate with different additive systems.

Conclusions

- Plastic recyclate is a raw material with potential
- Know-how and additives allow to optimize and improve properties of recyclates.
- Optimized additive packages create new value for recyclates
- The current study shows there is more to do.