A circular multilayer plastic approach for value retention of end-of life multilayers films

D1.10: Circularity by design guidelines for the next generation of recyclable films capable of substituting today's difficult to recycle multilayers

WP1: Systemic transition to the circularity of multi-layer films

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Abbreviations

PE: Polyethylene

PET: Polyethylene Terephthalate

PA: Polyamide

PP: Polypropylene

EVOH: Polyethylene vinyl alcohol

HDPE: High Density Polyethylene

LDPE: Low Density Polyethylene

PVC: Poly vinyl chloride

PVDC: Polyvinylidene chloride

AlOx: Aluminum Oxide

SiOx: Silicon Oxide

PO: Polyolefins

SEBSgMAH: Poly (styrene ethylene butylene styrene) grafted maleic anhydride

BOPPmet: Metallized bioriented polypropylene

PETmet: Metallized polyethylene terephthalate

MNL: multi nano layer

TD: Transverse direction

MD: Machine direction

NIR: Near Infra Red

rPE: Recycled Polyethylene

DfR: Design for Recycling

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Executive summary

The CIMPA project aims at developing a circular value chain for post-consumer multilayers, multimaterial packaging films and agricultural films. With this purpose, partners study and develop sorting, recycling, decontamination and upgrading technologies but they also have to consider the first step of the value chain, that is the design of the structure of the packaging.

Indeed, for several years now European countries have developed their own ways of assessing recyclability, based on their specific consumption mode, collection and recycling model, to give guidelines for their internal market and valorization path, leading European industries to be forced to consider each country, one by one when it comes to recyclability rules. These guidelines are necessary for the countries as specific consumption will lead to a specific mix of waste and composition into the bale and that is why most of DfR recommendations are the same in all countries. But sometimes there are specific rules depending on the collection & sorting streams, thus recycling processes & applications (color sorting, mix flexible PO, opaque PET…). This non-harmonized European map of guidelines led the industrial players to find new certification paths like RecyClass, that also have their own point of view on the different components of a packaging, but that may answer the question of recyclability more objectively and not considering only one country.

Today as the Plastic and Plastic Waste Regulation is being revised, we see a will of harmonization in the commission to be able to treat a common flow of waste that comes from packaging and every kind of plastics in the market. To face this challenge, the standards that will be created need some strong assessment of recyclability and sorting ability of the different kinds of structures and materials present today, considering the actual technologies, but it also needs to have an opinion on the possibilities that come with innovation. Moreover, this revision and the general European legislation on recycling rate and use of recycled material give high challenges to the industry, that needs to have some guidance on how to design a product to be recycled and reused in a sustainable, closed loop.

In this context the partners of the CIMPA project collected the information from the different work packages consisting of sorting and recycling technologies to build some guidelines on the use and the limits of the materials studied. To do so, a first map of European guidelines was drawn to depict the context and the actual differences that represent the points of interest to be studied. Then these guidelines were compared to the results obtained using the CIMPA technologies step by step (lab scale, pilot and industrial scale) to determine the added value of these innovations and finally new guidelines with some typical structures were explored.

Deliverable report

Introduction

According to the article 6 of the proposed revision of Packaging and Packaging Waste Regulation a packaging is considered recyclable if it complies with the following:

"(a) it is designed for recycling;

(b) it is effectively and efficiently separately collected in accordance with Article 43(1) and (2);

(c) it is sorted into defined waste streams without affecting the recyclability of other waste streams;

(d) it can be recycled so that the resulting secondary raw materials are of sufficient quality to substitute the primary raw materials;

(e) it can be recycled at scale. "[1]

Following this definition, the present guidelines for recyclability will focus on **three main steps of the value chain**: sorting, recycling, reprocessing. The process of designing the packaging will be addressed by the guidelines and the collection is a topic that should be addressed separately as it is a matter of communication, education of the consumer and logistics of collection.

As stated earlier, this report will first draw a picture of actual national or industrial guidelines for recycling that may exist in the EU. Once this basis is set an overlook on the work done in the CIMPA project according to the three topics of sorting, recycling and reprocessing at lab, pilot and industrial scale will be made. All this information will allow to finally define guidelines for the design of recyclable multilayer multimaterial films for food packaging.

Considering the scope of the CIMPA project that is about the multimaterial structures used in agricultural and food packaging application, this report will focus on guidelines for recycling when it comes to choosing: the base material of the design and the barrier material added to this structure. No work has been done over closure devices, labels, lamination adhesives, printing or other parts.

The information contained in this report includes the synthesis of the technical work realized by the CIMPA partners from lab scale with virgin grade polymers to industrial scale with recycled material from post-consumer waste. To demonstrate the results while keeping results confidential, most numerical values will be normalized to the ones of virgin grade PE film.

[1] According to «Proposal for a
REGULATION OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL
on packaging and packaging waste, amending Regulation (EU) 2019/1020 and Directive (EU) 2019/904, and repealing Directive 94/62/EC » Article 6 paragraph (2) p56

At the beginning of CIMPA project only flexible PE was taken into account as it was the most common recycling stream in Europe for flexible packaging. Today a new (for some countries) stream of flexible PP should appear, but it was not taken into account for the studies.

This report is an updated version of the first one published in 2023 (D1.2).

Map of the European Guidelines for Recycling

The different countries of the EU do not all have specific guidelines for recycling of flexible packaging. In this context and with the need of the industry to have indication on the recyclability of different designs many entities tried to answer the issue. The Table 1 is summarizing the different guidelines existing at European or national level with official guidelines and more theoretical ones (compilation of scientific knowledge and empirical trials).

		France (COTREP)	Austria (FH Campus de Vienne)	Central Agency Packaging Register	Recyclass	CEFLEX	Suez Circpack	network for circular plastic packaging
Base material	PE, all kind	recyclable	recyclable	recyclable	recyclable	recyclable	recyclable	recyclable > 90%
	PE Composites (mixture of different PE)	recyclable	recyclable	recyclable	recyclable	recyclable		
	Oriented PE	recyclable				recyclable		
	PE mixed with PP	limited recyclability	limited recyclability	limited recyclability	limited recyclability (<5%)	limited recyclability	limited recyclability	recyclable
	Other material	not recyclable				not recyclable	not recyclable	not recyclable
	PS, PVC, PLA, PET, PETG	not recyclable	not recyclable	not recyclable	not recyclable	not recyclable	not recyclable	not recyclable
Barrier	EVOH	Recyclable < 5% in PE stream	limited recyclability < 5%	Recyclable	limited recyclability < 5%	recyclable < 5%	limited recyclability < 5%	recyclable <2%, limited <5%
	Metallisation Al	limited recyclability (must not be on the external layer)	limited recyclability (must not be on the external layer)	Recyclable	not recyclable	recyclable < 5%	limited recyclability	recyclable
	AlOx, SiOx	limited recyclability	Recyclable (without topcoats or precoat)	Recyclable	Recyclable	recyclable < 5%	recyclable	recyclable
	carbon coating using plasma		Recyclable				recyclable	
	PA	Not recyclable	Not recyclable	Considered recyclable with	limited recyclability (2)	recyclable < 5%	Not recyclable	Not recyclable
	Aluminium lamination	Not recyclable	Not recyclable		Not recyclable	Not	Not recyclable	Not recyclable
	Other material	Not recyclable		Not recyclable	Not recyclable	Not	Not recyclable	Not recyclable
	PVOH	limited recyclability		Not recyclable	Not recyclable	recyclable <	Not recyclable	recyclable
	PVC	Not recyclable	Not recyclable	Not recyclable	Not recyclable	Not	Not recyclable	Not recyclable
	PVDC	Not recyclable	Not recyclable	Not recyclable	Not recyclable	Not	Not recyclable	Not recyclable

(1): nylon 6 or co-polyamide 6-66 in coextruded PE/PA films without EVOH, combined with MAH-grafted PE as an adhesive promoter at a ratio of at least 0.5 g of adhesive per 1 g of PA
(2): ≤15% PA 6/66 copolymer with melting temperature < 192 ºC and incorporating ≥ 10% PE-g-MAH tie layers

Table 1. Summary of European guidelines on flexible packaging concerning base and barrier material[2,3,4,5,6,7,8].

[2] According to COTREP recommendations (https://www.cotrep.fr/etapes/films-souples-complexes/fs-pebd/)

[3] According to FH CAMPUS WIEN, **CIRCULAR PACKAGING DESIGN GUIDELINE,** DESIGN RECOMMENDATIONS FOR RECYCLABLE PACKAGING; Version 04, October 2021; APPLIED LIFE SCIENCES

[4] According to Zntrale Stelle VERPACKUNGSREGISTER, Minimum standard for determining the recyclability of packaging subject to system participation pursuant to section 21 (3) VerpackG

[5] According to Recyclass recomendation, (https://recyclass.eu/recyclability/design-for-recycling-guidelines/)

[6] According to CEFLEX recomendation, (https://guidelines.ceflex.eu/guidelines/)

[7] According to SUEZ CIRCPACK, Design for recycling guidelines 23.04.2019

[8] According to the network for circular plastic packaging, Reuse and recycling of plastic packaging for private consumers

This summary helps CIMPA partners to understand which points in the design of a film are already confirmed as being recyclable or not recyclable and on which material there is no consensus in the market.

First of all, it has been identified that these guidelines are based on the polyethylene stream, which makes sense as it is the main component of the flexible packaging film. Although some of these guidelines also consider polypropylene, the guidelines are similar to those of PE. This is mostly because the collection, sorting and recycling produce a mixture of PO (PE & PP) in the country.

When it comes to the points of agreement of all these guidelines, it appears that a base material consisting of any kind of PE and in different mixes (HDPE + LDPE) is accepted if there is at least 90% of polyethylene (or polypropylene if the stream exists). All the other materials consisting generally of PET or paper are recognized as not recyclable.

For the barrier layers there are also common results. Indeed, limited compatibility for the metallization for example as long as the packaging is not natural, as it does not represent a too large amount of the structure or as it is not placed on the external part of the packaging (skin layer) for sorting issues. The main issue for internal metallization is the color of the final product. Other kinds of surface treatment as aluminum oxide, silicone oxide or carbon oxide deposition are accepted if they are not used with coatings used for protection or adhesion promotion (topcoat or precoat). Other agreements are found over PVC, PVDC, aluminum foil or other kinds of material that are considered as not recyclable. For EVOH, it appears that all the guidelines indicate this material as recyclable as long as it represents less than 5% of the total structure, however it is to be noted that some also consider the EVOH content not in the film itself but in the total stream to allow some structures with > 5% EVOH and avoid a switch with less EVOH and additional other resins.

When it comes to the points of disagreement in these guidelines, they are limited to three interesting points:

- PE/PP mixability: Respecting the base material, it looks that a consensus was not found on the mixability of the polypropylene with polyethylene. This disagreement surely comes from the variety of grades and molecular architectures existing in the market of these two materials and final applications and requirements in different countries;
- PVOH barrier material: Some recommendations do not consider it as recyclable and others do but this surely comes from the new applications in which this material is used. Indeed, it is more and more used as a coating in different mixtures to give barrier properties to new designs. This material is also often soluble in water and may interfere with the recycling or sorting processes that use water (cleaning, density sorting, cooling). Deeper studies should be led to determine the recyclability of these new coatings;
- PA barrier layer: Polyamide barrier layers is surely the most discussed point when it comes to recycling of the flexible films. Depending on the kind of polyamide and polyethylene used, the recycling results (in terms of quality and reusability) can change a lot, and this makes the choice difficult. This

family of barriers needs to be more studied and specified. Moreover, the polyamide is hardly recognized in sorting processes (preventing it from being sorted out of the mixed stream) and this material is constantly improved by the suppliers making this stream very heterogeneous in Europe and in the different applications where it is used.

To conclude on existing guidelines, they all recommend **to change from multimaterial to mono material structures**. This switch in design would definitively help to recycle most of the common structures. Nevertheless, many of the food packaging or agricultural films need oxygen barriers to protect its content against oxidation or avoid fumigation gases to escape. This need of oxygen barrier cannot be achieved with the same polymer as the base one (polyolefins) and some specific applications also need high thermal properties (pasteurization, high production rates) that cannot be achieved using mono material structures. In this context flexible packaging and agricultural film designers need to have recyclable resins to achieve these high demanding properties. As regard of oxygen barrier, EVOH seems to be the best option as it is recognized as recyclable under 5% rate of the structure. Mixtures of PP and PE could, if proved to be recyclable, achieve high temperature resistance properties. The study of the real impact of PA could also be important as it has interesting properties as oxygen barrier and mechanical performance as well as PET-PE structures recycling could allow to keep this very efficient structure for high demanding applications.

CIMPA partners have studied 4 streams of flexible multimaterial polymers consisting of:

- PE/EVOH/PE stream
- PE/PA streams
- PE/PET stream
- Metallized or metal laminated polyolefinic based structures.

According to the aforementioned definition of recycling stated by the EU commission, a recyclable polymeric film should be sortable, recyclable and be able to be used in the same application as the first product, and all of the above must be demonstrated at scale.

Sorting of the film:

In CIMPA, partners worked on the sorting ability of the streams mentioned before.

At lab scale, for instance, each one of these materials could be detected using thermal analysis or spectrometry. When it comes to industrial scale sorting, the most common technology is NIR spectrometry as it handles high industrial throughputs. Even though this technology is very efficient, it cannot differentiate all multilayered structures. Within the scope of CIMPA, the company PELLENC ST has been able to develop its NIR technology, using both virgin and post-consumer material. Therefore, thanks to CIMPA's study, they succeeded in separating PE/PA (all kinds of PA are mixed) and PE/PET films from the actual post-consumer waste stream.

CIMPA sorting trials also demonstrated that the combined deployment of PELLENC ST NIR technology and FILIGRADE's CurvCode digital watermark enables effective sorting of complex multi-layer materials. Digital watermarking also makes it possible to sort on criteria not-related to material-structure like 'food versus non-food'.

These trials were performed at industrial scale and allowed CIMPA partners to define PE/PA and PE/PET as sortable. Moreover, another learning is that all the metallized or metal laminated layers can also be sorted using induction separation even though they will be sorted with other metallic contaminants such as aluminum cans (additional sorting step or technologies needed).

The last structure consisting of PE and EVOH cannot be separated yet. This is not an issue today as EVOH is recognized as recyclable with PE under 5% use rate (usual rate in present structures). Even if it is not an issue EVOH could be sortable using new technologies. Indeed, the CurvCode technology from FILIGRADE studied in CIMPA has proven with the sorting demonstrator that PE/EVOH used in food packaging applications could be sorted out from the stream and used in a specific recycling path like the one designed in the project.

CIMPA studies at laboratory to pilot scale

Recycling technology on virgin material

PE/EVOH, PE/PA and PE/PET streams are studied in mechanical recycling path consisting of the steps below:

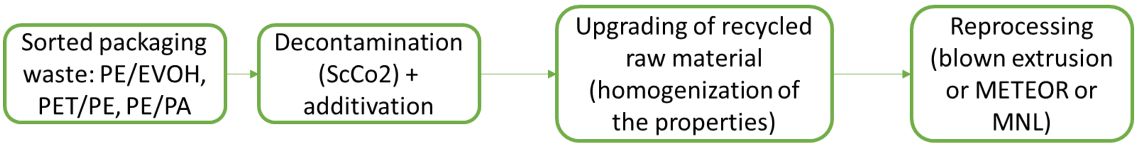
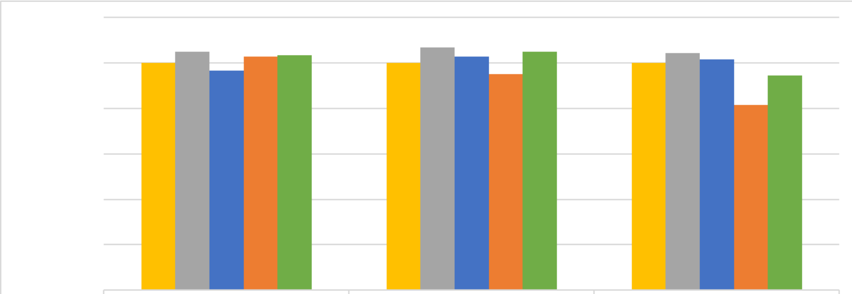


Figure 1. Flow chart of the packaging waste streams in mechanical recycling.

When it comes to metallized PO the chosen technology is dissolution, considered as physical recycling because metallized coloration cannot be removed with mechanical recycling. Furthermore, dissolution is able to separate the PO from the other polymers present in the structures. Some trials were also run to establish the effect of polyamide, EVOH and PET.

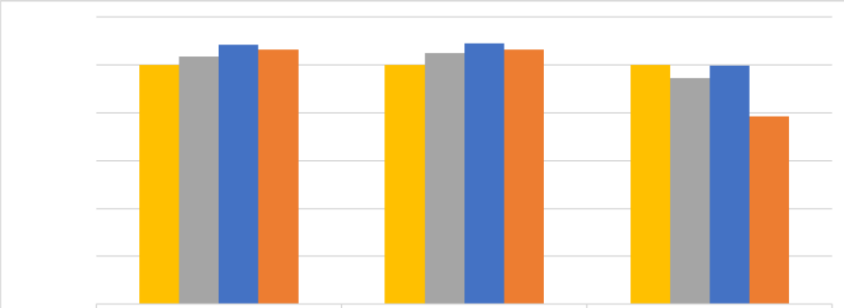
Mechanical recycling

Mechanical recycling was first studied over virgin material in the upgrading step at VTT with their VAREX compounding process followed by lab scale cast film extrusion. The used material did not go through washing, densification nor flotation which are also important steps that will be studied further in the project (washing and densification only). The process used here was based on blending different granulates of the studied material: EVOH 32%mol of ethylene, PA (6/66) and PET with different rates of LDPE and possibly compatibilizers. The used EVOH is a 32% ethylene commercial grade while the PA is a copolyamide 6-6;6 also a commercial grade. The utilized commercial PET copolymer grade was formulated for injection/stretch blow molding. The films obtained by cast extrusion were then biaxially stretched 3.5x3.5 times. The mechanical properties of the obtained films were finally analyzed.



	Modulus (%)	Strain at break (%)	Elongation at break (%)
Pure PE	100	100	100
3.1% EVOH	105	107	104
5% EVOH	97	103	102
6.9% EVOH	103	95	81
7.5% EVOH	103	105	94

Figure 2. Evolution of mechanical properties in function of EVOH content, normalized to PE film



	Modulus (%)	Strain at break (%)	Elongation at break (%)
Pure PE	100	100	100
7.5 % PA	103	105	94
15 % PA	108	109	99
22.5 % PA	106	106	78

Figure 3. Evolution of mechanical properties in function of PA content normalized to PE film

These trials demonstrated that adding secondary materials to virgin PE does not influence the mechanical properties a lot even if we can see a little decrease in blends containing 5% and more EVOH and a slight decrease in elongation at break for all the samples containing PA. These first results are in line with actual European guidelines knowing that PA is impacting the film's elongation at break, even at low concentration (even if upgrading the other properties) while EVOH does not impact the properties under 5% rate.

All these studies were performed using actual compatibilizer agents (LLDPE grafted maleic anhydride). The PE/PET stream has also been studied using compatibilizer being SEBS-g-MAH.

The PET/PE recycling with compatibilizer also showed good mechanical properties even if it was about 95% of the one of PE/PA films however this blend also showed a very white appearance, surely because of the PET phase and the number of defects was also higher than the ones present in PE/PA blends (on some samples twice more).

To conclude on this recycling part, the results from CIMPA looks aligned with actual guidelines knowing **that EVOH does not impact the PE stream under 5% rate of the formulation**, PA can impact some properties but needs deepen study. The only point that is astonishing, when compared to state-of-the-art studies, is that PET does not seem to impact PE recycling quality. These results come from three points: First, for the trials we compatibilized PET and PE using actual commercial grade of SEBS grafted with maleic anhydride, This additivation is not present in today methods of recycling and if PET/PE had to be considered, compatibilizing could surely be a topic as it is today for PA or EVOH. Then, the trials were led with virgin material, we also think that a mixture of different PET and PE added to the degradation due to the life of the packaging should change the results. It is also to be noted that the use of compatibilizers in the blends was beneficial to reach these properties.

The conclusions on these results must be considered carefully because:

- Only extrusion step has been done here without considering the other recycling steps (washing, floatation, drying, filtration Etc.). Moreover, only basic mechanical analysis on films has been studied (modulus, strain at break and elongation at break) whereas many more parameters should still be considered: floatation, humidity uptake, filtration behavior (clogging, more losses), sealing ability.
- Only virgin material with known and constant mixture of material was used with only one kind of PA6/66 or EVOH 32%.
- Studied process was about blending virgin pellets and not recycling actual films.

Physical recycling:

The first studies on physical recycling were performed on post industrial waste, meaning that the source of the wastes containing metallized PO (BOPPmet/PP and PETmet/PE) come from the partners (Leygatech, Barbier Group and Eversia). Both the pure streams and mixes of them have been studied at lab scale on the installation TNO Möbius 1.0 at TNO. This stream may of course also contain PET or other materials as the goal here is to dissolve and recover only the PO fraction (mix of PE and PP).

The results obtained were very satisfactory as the yield of recovery of 84% and 85 % with respect to PP and PE fraction respectively were achieved. Moreover, no Aluminum nor PET could be found in the recovered PO material which indicates a good purity even though recompounding induced a bit of discoloration of the material.

Other materials have also been studied in physical recycling to see what could happen if the stream with metallized foils contains EVOH or PA. **It appears that even at low level of EVOH (5-10%) PE and EVOH cannot be separated through dissolution while for the PA the threshold is more around 15% and also mainly affects the yield while the PO product is relatively pure PO.**

Reprocessing of virgin upcycled material:

The mechanically recycled streams have first been reprocessed at lab scale using virgin material over innovative technologies that are METEOR (extensional flow mixing coupled with cast extrusion) and multi nano layering also coupled with cast extrusion. In the second period (that has begun), partners are studying the real packaging wastes of these streams, after upgrading, over these innovative technologies, at pilot scale but they will also use these streams with real industrial process that are blow film extrusion at industrial partner's plant.

PE/PA

As mentioned before PE/PA (6/66) was studied using METEOR and MNL technologies and with virgin material consisting of the same grades than the one used in upgrading process.

With METEOR, the results that we faced were similar to the ones after upgrading. Indeed, PE/PA blends have their elongation at break in machine direction decreasing while increasing the PA rate, with or without METEOR even if it allows to have better results (see figure below). When talking about the elongation at break in transverse direction this property decreases until 15% of PA where it improved by a factor of 20 before a slight decrease at 22.5% of PA.

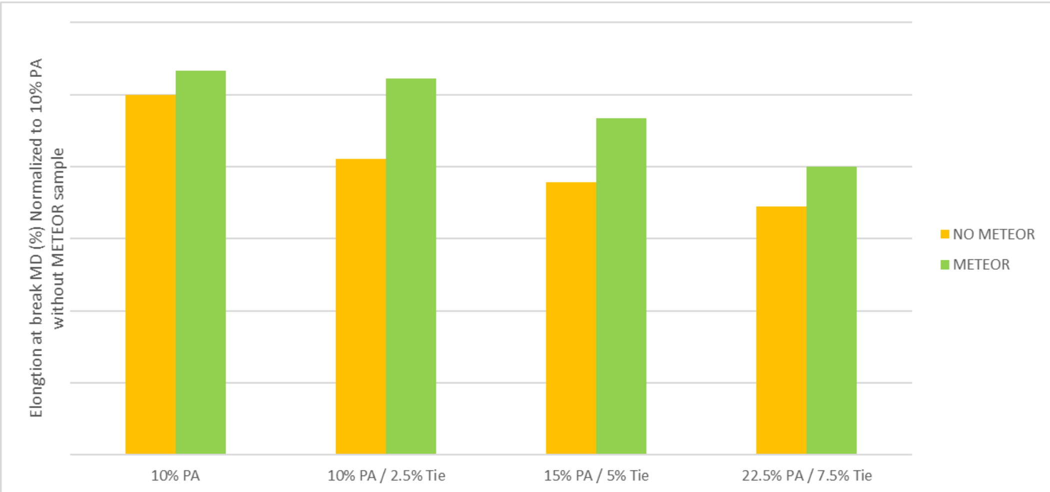


Figure 4. Elongation at break of PE/PA blends in machine direction, with and without METEOR (normalized to PE/PA blend at 10% without METEOR).

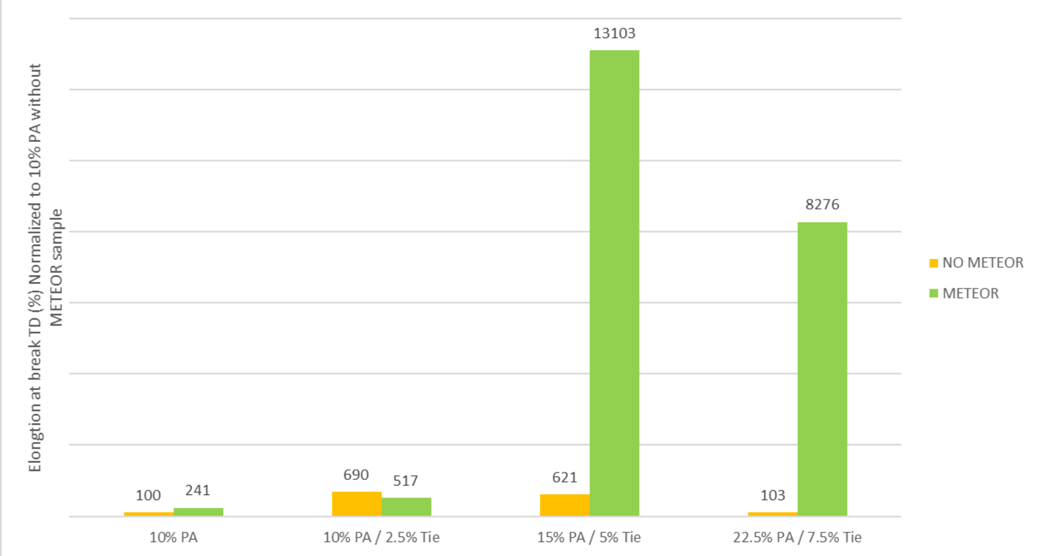


Figure 5. Elongation at break of PE/PA blends in transverse direction, with and without METEOR (normalized to PE/PA blend at 10% without METEOR).

PE/PA has also been reprocessed using MNL technology where it performed in a totally different way. Indeed, here all of the mechanical properties decreased with increasing PA content. Nevertheless, thanks to this technology we obtained good barrier properties, in the range of what is used in the market today.

This difference in properties according to the material is well understandable as in MNL PA layers are very thin (decreased mechanical properties) but continuous (improved oxygen properties). It is almost sure that trials with real packaging waste from PE/PA will give different results as the PA will not be in a separate matrix but it is interesting to see here that, in a blend, PA 6/66 still allows PE recycling thanks to METEOR process and the next study with MNL and real wastes should also be interesting.

PE/EVOH

Cast and METEOR experimentations with PE/EVOH (32%mol of ethylene) blends showed similar results as the aforementioned ones knowing that the mechanical properties of the films are stable until we reach a rate of EVOH of 5% where it begins to decrease. Still, it is interesting to notice that we can clearly see an influence of tie resin that clearly helps PE/EVOH blend to get compatible.

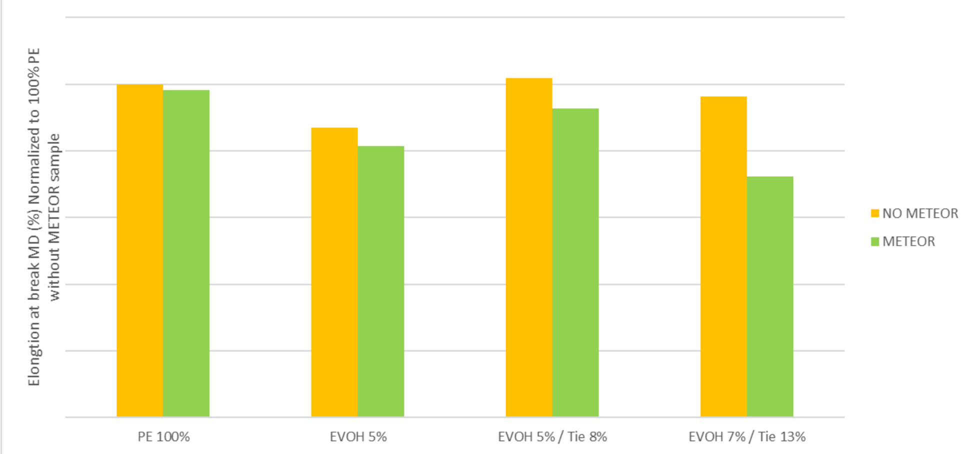


Figure 6. Elongation at break of PE/EVOH blends in machine direction, with and without METEOR (normalized to 100% PE without METEOR).

When it comes to MNL technology the results are similar to the ones achieved by PE/PA. Indeed, the reduction in mechanical properties becomes more pronounced when the number of layers increase.

PE/PET:

Finally, PE/PET blends went through the same process as PE/EVOH and PE/PA. In METEOR, first, the results showed an important decrease in elongation at break when not using compatibilizer, of about 70% for 10% PET in the blend. When using some coupling agent, the results were more stable (while still decreasing) with a loss of about 15% of the elongation.

A multinanolayering (MNL) process has also been used for PET and PE but for now it has not been successful and other trials should follow.

CIMPA demonstration at industrial scale on real packaging waste

Recycling technology on real conditions

After these first steps, the real waste streams that were collected in PAPREC facilities and sorted at Pellenc facility were used when possible and post industrial waste when no other choice was available. The used streams were:

- PE/PA from household waste and from post industrial waste;
- PE/PET from household waste;
- PE/EVOH from post industrial waste;
- Metallized polyolefins from household waste.

The three first streams were used for decontamination and upgrading process, at AIMPLAS and VTT, respectively, and were finally shipped to LEYGATECH and BARBIER GROUP for demonstrator production. The Metallized stream was used at TNO facilities to produce the physically recycled polyolefin blend that was also upgraded at VTT before its reprocessing at BARBIER GROUP.

PE/PA and PE/PET stream from household waste were characterized to determine their concentration in PA or PET as well as their thermomechanical properties. The results are shown below in Table 2.

Material	Approximate DSC composition [%]				OIT [min]		MFI [g/10 min]					TGA ash content
	PE	*PP*	*PA*	*PET*	*210 °C*	*255 °C*	*190 °C/ 2.16kg*	*210 °C/ 5kg*	*230 °C/ 5kg*	*255 °C/ 2.16kg*	*255 °C/ 5kg*	*[%]*
r-PE/PA	90.7	2.5	6.7	-	11.8	-	-	NF	6.95	-	-	2.74 ± 1.42
r-PE/PET	88.7	3.9	-	7.4	23.7	1.46	-	-	-	3.1	23.9	7.50 ± 1.41

Table 2.Characterization of the post-consumer recyclates before VAREX upgrading. Approximate polymer composition was derived from the DSC melting enthalpy. Oxidation induction time (OIT) was measured by DSC, indicating the thermal stability of the material at given temperature. MFI is the melt flow index. NF denotes no flow in MFI test. (from D5.1)

PE/PA and PE/EVOH from industrial wastes were also characterised by DCS to know their concentration in PA and EVOH, the results are shown below. The PA in this stream is a copolyimide 6/6,6 and the EVOH is a 32%mol of ethylene grade.

Material	Origin	Composition [%]			
		(L-)LDPE + tie	*PA6-66*	*EVOH*	*PET*
r-PE/PA	**LEY & BAR** (post-industrial waste)	81.3	18.7	-	-
r-PE/EVOH	**LEY & BAR** (post-industrial waste from several batches)	93.2	-	6.8	-

Table 3. Description and estimated composition of the post-industrial multi-layer waste before upgrading

Mechanical recycling:

After their preparation (shredding, washing and drying) at AIMPLAS, both batches of PET/PE and PE/PA from household waste were sent to VTT for upcycling. For batches coming from post industrial wastes, these were sent to VTT from industrial partners directly in pellet form ready for upcycling.

Only general information will be given here as more technical and detailed data are available in public deliverable 5.5 and in deliverables 5.1 and 5.6.

During the upcycling process, online viscosity measurement was conducted and extrusion parameters (mostly temperature) were fine tuned to ensure a stable and homogeneous flow. The first important difference between the different batches was on extrusion temperature. Indeed, for PE/PA and PE/EVOH extrusion temperature was set at 210°C while for PE/PET we had to increase that temperature to 255°C to melt the PET phasis. This change in extrusion parameter has a direct impact on viscosity behavior of the blends that is added to the intrinsic material behavior. For both of these reasons, extensional and shear viscosity of PE/PET blends were measured way lower than the ones of PE/EVOH or PE/PA as shown in Figure 7.

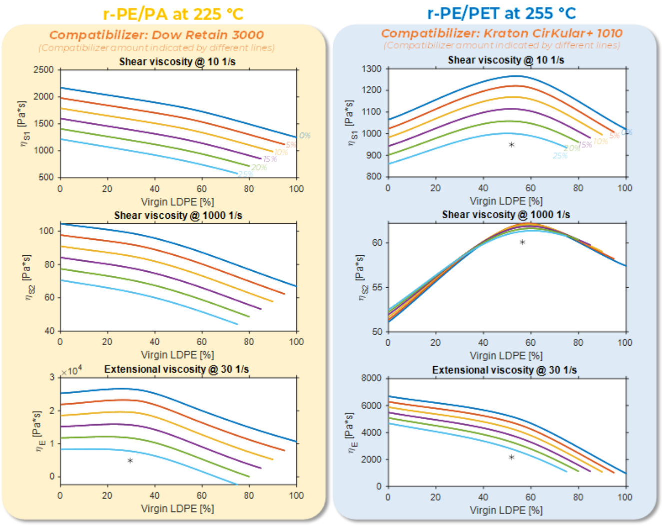


Figure 7. In-line VAREX viscosity modelling of post-consumer r-PE/PA and r-PE/PET blends (modelled melt viscosities at various shear and extensional rates). The individual lines correspond to different compatibilizer concentrations. (From D5.1)

These values give us first information for the reprocessing as viscosity is an important parameter for blown film extrusion. The fact that PE/PET blends are more fluid risks to be a problem for the reprocessing step, moreover at this process temperature of 255°C the degradation risk of the material is higher (see OIT column in Table 2).

The in-line viscosity adaptation of VAREX process was applied to every blend and led to very homogeneous material ready for the next step. No difficulties were noted by VTT. During this step compatibilizers were added as described in deliverable 5.1 considering the nature of the material. More precise trials were made over PE/PA and PE/EVOH blend considering different compatibilizer to determine which kind of material was giving the best performance. This study is present in the next section of this document.

Finally, the up-cycling of post-industrial waste showed good results managing to reach a reduced variance in viscosity distribution when compared to the input waste as shown in the figure below.

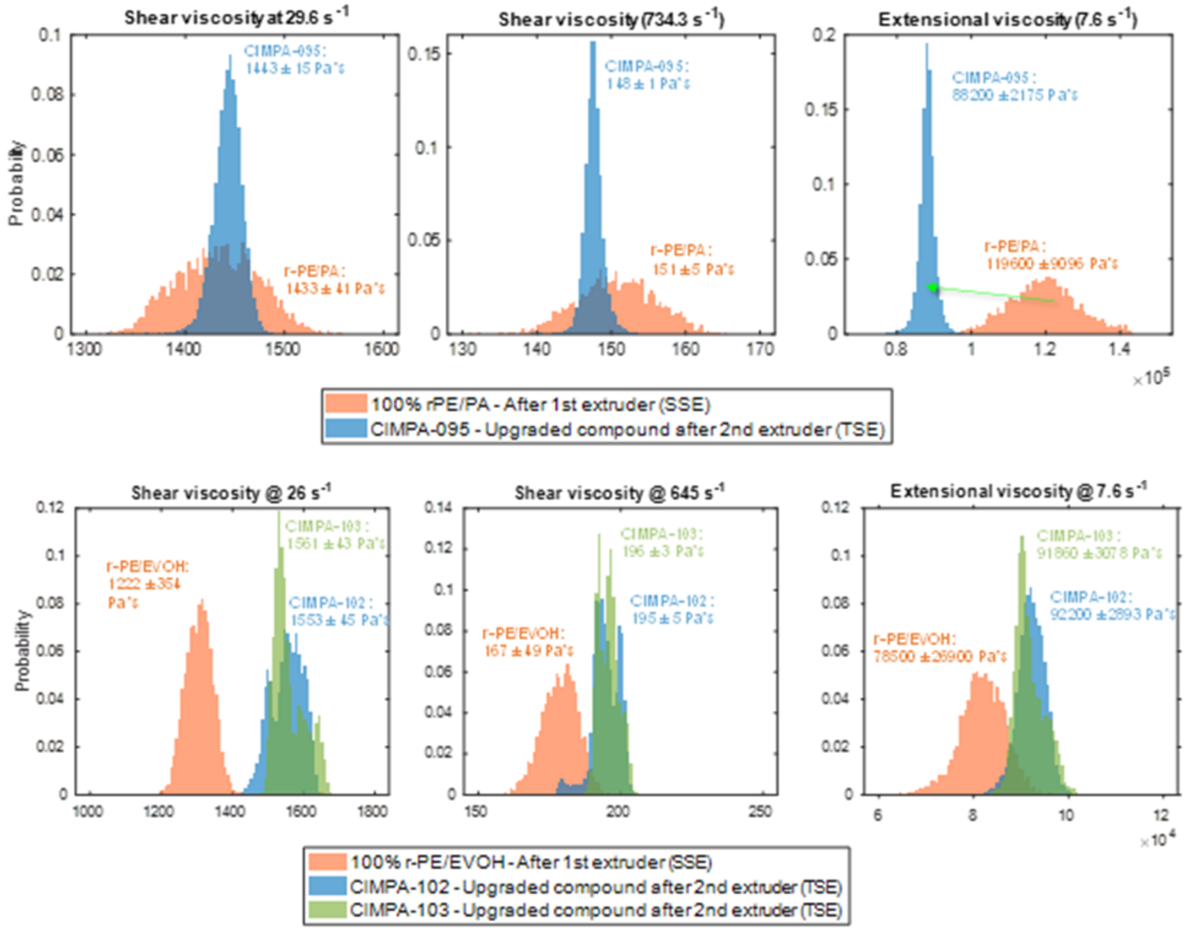


Figure 8. Feedstock variation of r-PE/EVOH and r-PE/PA post-industrial waste before and after VAREX compounding (from D5.1).

As a conclusion for this step all the material were successfully upcycled and reach a good viscosity homogeneity. The only possible source of issue for the next step is the temperature of process and the viscosity of PE/PET batch as it risks to degrade in the reprocessing and to be difficult to blow.

Physical recycling

The metallized stream from household waste was characterized to determine its composition (se details in D4.4), it appears that this batch contains ~56% of L-/LDPE, 35% of PP and ~9-12 % PET. As planned during the first steps of the project, no EVOH nor PA is measurable so there should not be any issue during the dissolution process (see section on physical recycling in the chapter dedicated to first trials overs virgin material). These wastes were then dissolved in MÖBIUS apparatus at TNO and filtered to recover the polyolefin fraction as explained in the figure below.

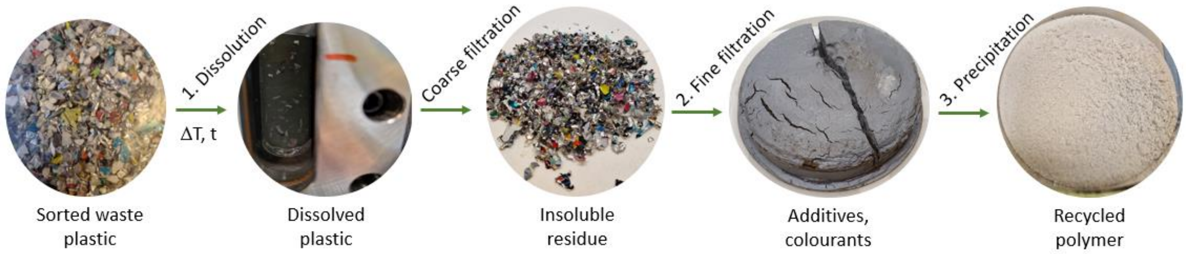


Figure 9. Scheme of the Möbius apparatus steps (from D4.6)

This step was performed at higher TRL than the first trials, as TNO built a pilot MOBIUS plant for TRL 5 process to recycle this batch. Some challenges were encountered during the processing as the gelation of the polyolefins creating difficulties for the recovery of the polymers. To overcome this challenge on time, final filtration was pulled of the process giving a greenish powder after dissolution. This issue allowed TNO team to understand some phenomenon in their process and will allow them to consider ameliorations in future upscaling.

Once the dissolution was over, the batch was characterized and the concentration of PP was of around 20%. This decrease, when compared with previous characterization was explained by TNO team by the fact that PP is less soluble in the solvent and there is surely a part of it stuck in the gel that is created in the process.

Finally, this powder was re-compounded for stabilization and compatibilization of PE/PP while also stabilized in viscosity in the VAREX process. The final produced blend contains 20% recycled PO and is ready for reprocessing.

It seems that operating physical recycling at higher TRL over household waste is complicated even if it gives higher quality material than mechanical recycling (considering that it only keeps PO fraction). This technology is interesting but pollutants such as organic varnish (PVOH for example) or barrier layers (EVOH, PA) may cause gel issues in this process. For such reason, we consider it should only be used over metalized films that should not contain any polar or partially soluble material.

Study on the effect of compatibilizer:

Lab scale studies, exposed at the beginning of this report, showed us that compatibilizers can help in getting better properties from recycled blends. To better understand the differences between the proposed grades on the market, CIMPA partners decided to include a screening study on the different existing technologies of compatibilizer. As this decision was made near the end of the project, these agents were only compared at iso concentration in the blend. The impact on concentration of these agents in the blends was not explored and actual recommendations were considered for the guidelines.

Seven different existing material were studied over the blends of PE/PA and PE/EVOH, both coming from post-industrial wastes as these are more homogeneous and with a known concentration in EVOH or PA. All these agents of compatibilization are based on the presence of maleic anhydride, present via copolymerisation or by grafting process, these materials differ by their base material and concentration of aforementioned active group. No names are given here but these agents are all active commercial grades from 6 different supplier.

PE/PA/compatibilizer blends were prepared by VTT using their VAREX process and transformed into film by BARBIER GROUP with their monolayer pilot line while PE/EVOH/compatibilizer blends were dry blended just before extrusion on same pilot line.

The first results from PE/EVOH blends (see below Figure 10) show us that, adding compatibilizer allows to improve the elongation at break of 20 to 50% while keeping stress at break constant which could indicate a better adhesion of EVOH phasis in the PE matrix. The variations between the different blends could also be explained by the differences in base materials used for compatibilizers.

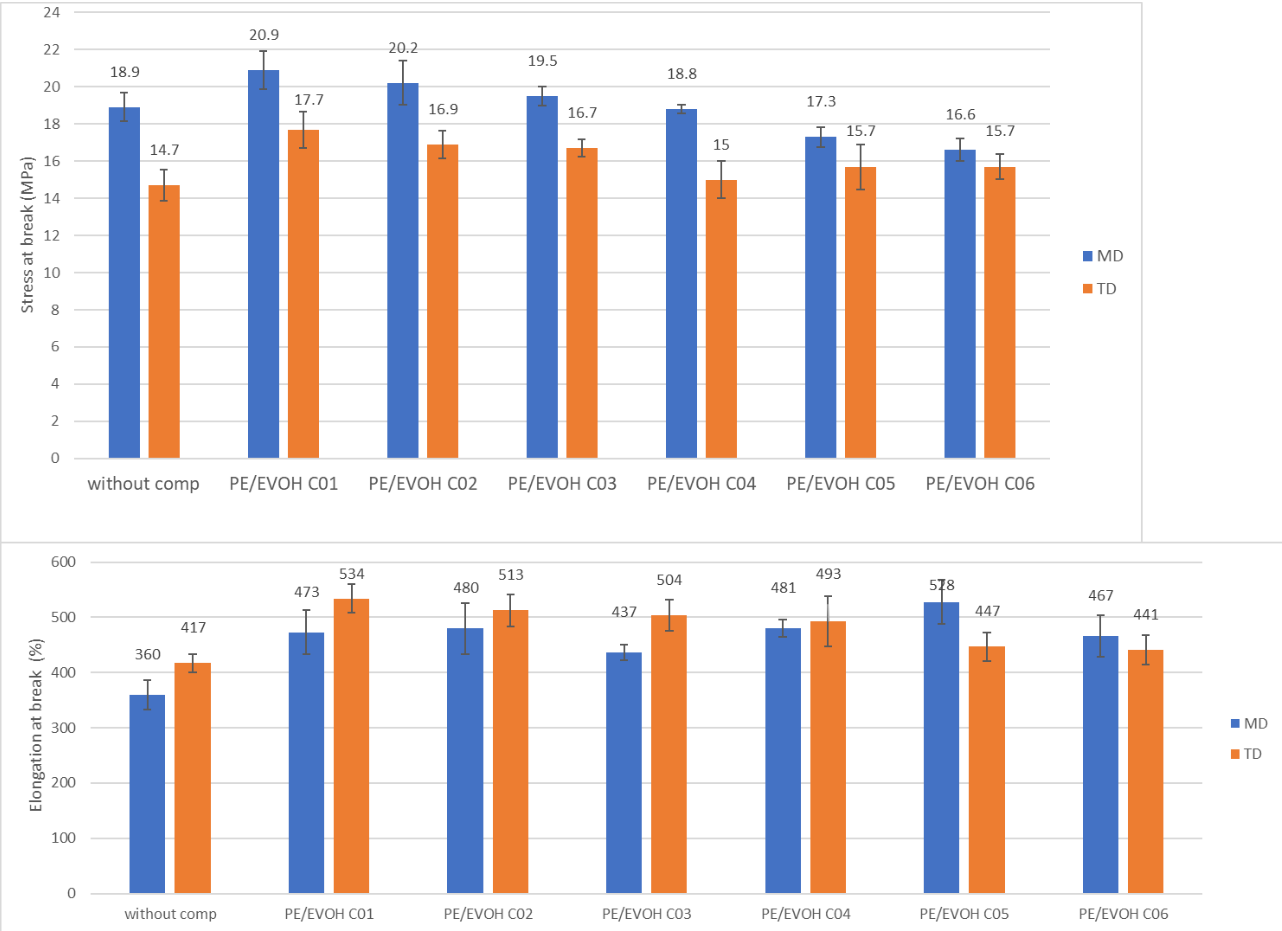


Figure 10. Elongation and stress at break of 70µm films prepared on pilot monolayer blown extrusion line with blends of rPE/EVOH with different compatibilizers.

For rPE/PA, we see that stress or elongation at break are not really impacted by the addition of compatibilizer, only the transversal elongation is improved while the three other values stay constant. Still when analysing impact resistance, measure via dart drop test, we notice an improvement of about 30 to 230% of the resistance of the film. Even if the addition of some virgin material could explain a little improvement, the concentration of compatibilizer here is below 5%w, so we can also conclude that compatibilizers increases the blend performances.

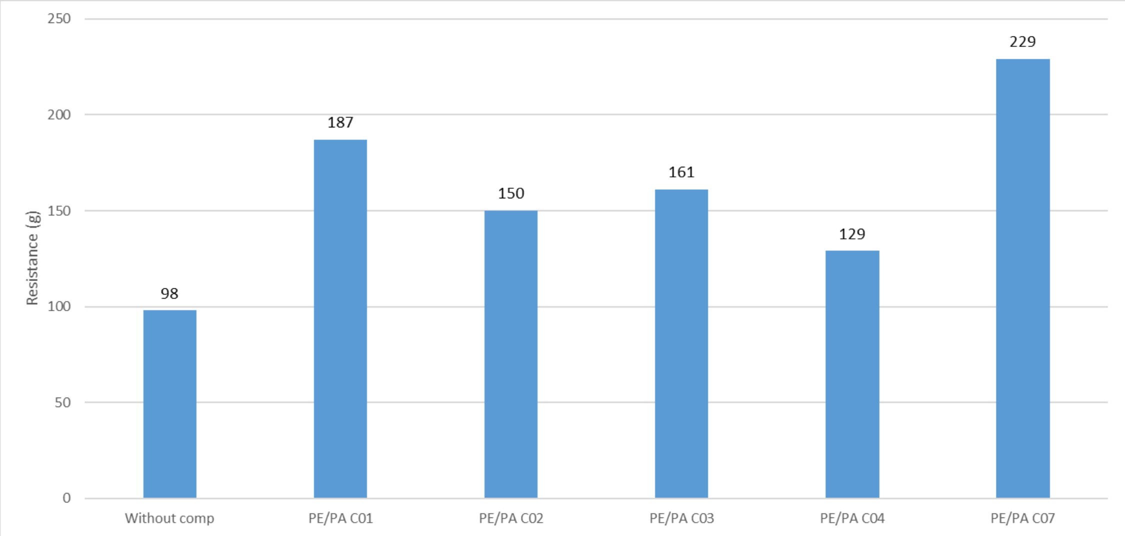


Figure 11. Impact resistance of the 70µ films produced on a monolayer blown extrusion pilot line using blends of rPE/EVOH with different compatibilizer.

The results presented before tend to prove that adding compatibilizer gives better mechanical properties to the blends, still it looks like the differences between the compatibilizers cannot be attributed to a technology difference nor a concentration in maleic anhydride groups but it could very well come from the base material.

Reprocessing of upcycled material:

The four upcycled blends were then reprocessed at industrial or pilot scale by BARBIER GROUP and LEYGATECH.

The rPO batch, coming from physical recycling and blending at TNO and VTT (respectively) was reprocessed at pilot scale by BARBIER GROUP into a typical lamination structure. The mechanical properties of the film with a concentration of 10% of recycled material did not change and even some improvement could be found surely thanks to the mixture of polyolefins. The only issue with this material was its green tint that comes from an insufficient filtration in recycling process. This issue should be fixed in next upscaling.

PE/PA and PE/PET, both from post-consumer waste, were reprocessed in a monolayer structure at BARBIER GROUP facilities at 30% recycled content. Results are interesting as they show that PET/PE blend is not disturbing the film structure more than PE/PA one as they both make the structure more rigid and brittle when compared to the same structure with LDPE recycled content (rPE(silage)).

Material	Thickness [µm]	Stress at break [MPa]		Elongation at break [%]		Tear resistance [cN/µm]		Dart test [g]
		MD	TD	MD	TD	MD	TD	
rPE (silage)	55 µm	17.8	15.5	284	571	2.7	10.6	67
rPE/PA	54 µm	12.7	11.0	218	530	2.7	15.6	39
rPE/PET	46 µm	14.9	13.7	184	519	2.1	9.9	45

Table 4. Tensile, tear and dart results of the blown film demonstrators using upgraded r-PE/PA, r-PE/PET and r-PE (silage) materials. The recycled content is 30%. Measurements performed by BARBIER GROUP.

Even with this degradation of the film properties, the film can still be used and the recycled material did not cause any perturbation of the process which means that at low concentration these blends can be used in actual films produced in the industry for bag application but it seems difficult to consider using recycled materials at 100%.

PE/PA and PE/EVOH from post industrial wastes were also reprocessed. The first one was extruded by BARBIER GROUP at 40% in the core layer of a typical silage film structure, at industrial scale. This extrusion shows that mechanical properties are not very impacted when compared to virgin material, only the tear resistance looks higher with PA content and even higher if VAREX process is used compared to PE/PA not upcycled.

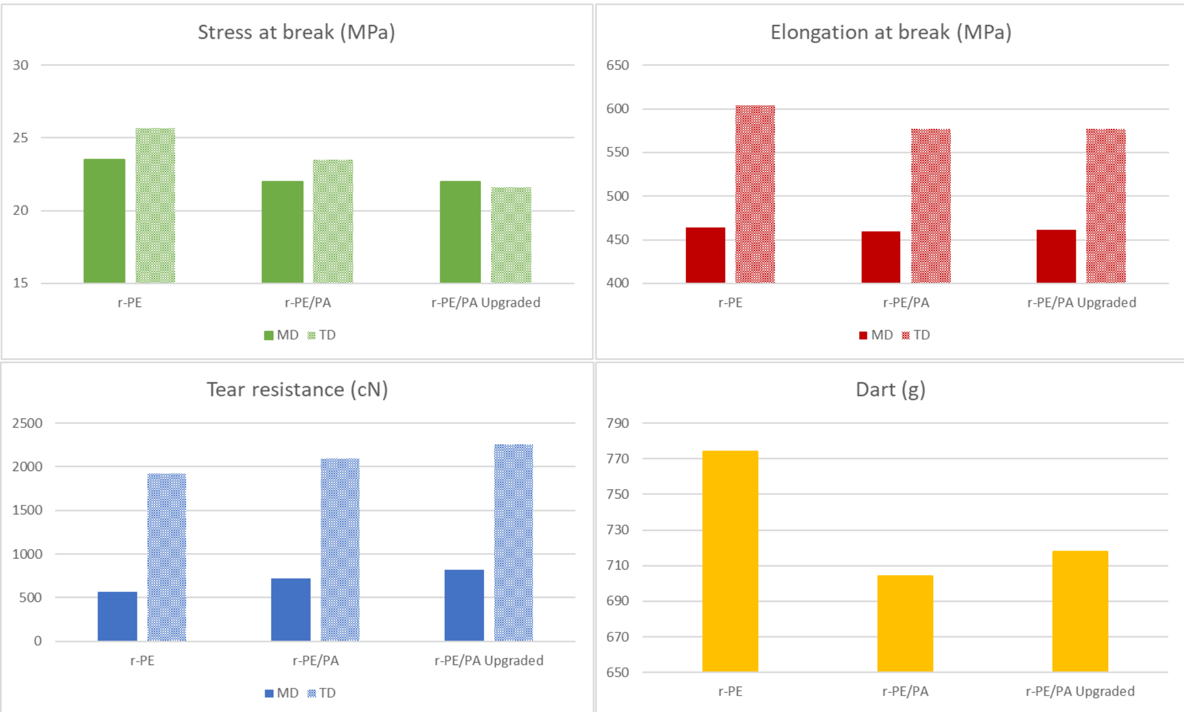


Figure 12. Mechanical properties of the industrial demonstrator films using upgraded post-industrial r-PE/PA

Moreover, ageing of these films was realized to determine their ability of being used for silage application. The graph below shows that addition of rPE/PA does not impact the UV resistance, in fact it looks even better than the reference.

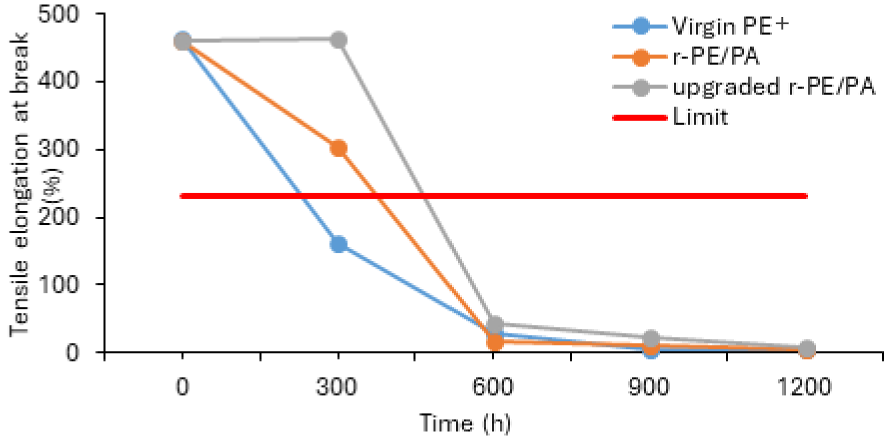


Figure 13. Effect of UV-ageing on the tensile mechanical properties of the demonstrator films

For the PE/EVOH blend, it was used in typical white lamination structure (as the industrial waste was white) with an oxygen barrier layer at a concentration of 10% in the final structure. As before the demonstrator was compared to a structure containing only virgin material and to another one containing 10% recycled material that did not go to upcycling. The results are about the same as before, there are no deviations of the mechanical properties here and neither for the barrier properties. We see the impact of the upcycling when compared with "ref recycled" material as modulus in MD and TD increase when the material is upcycled.

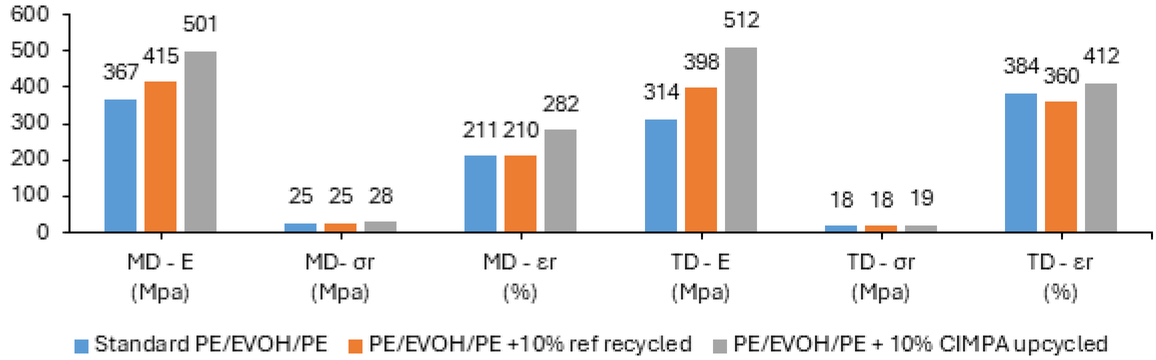


Figure 14. Comparison of the tensile properties of the CIMPA PE/EVOH/PE demonstrator versus standard and reference structures. (E for Young modulus, σ for strain and ε for deformation)

Considering these results CIMPA partners decided to try different concentration of rPE-EVOH in a mono layer formulation, at pilot scale in BARBIER GROUP facilities.

These trials (see Figure 15) show that the main impact of rPE/EVOH blend is over dart drop test that decreases directly when increasing the recycled content. Still, the other properties do not vary too much until a concentration 50%, if this concentration is overpassed the material could still be used for other purpose like bag fabrication as the properties are comparable to the ones of the first demonstrator presented in this section (see Table 4).

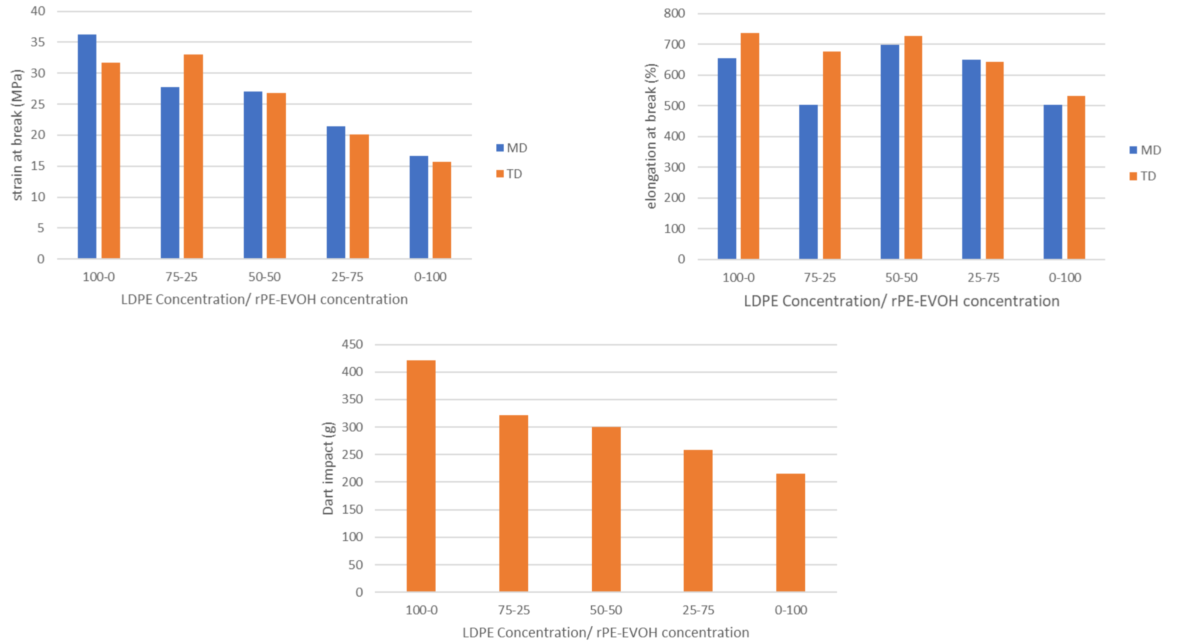


Figure 15. Mechanical properties of film with different concentration of rPE/EVOH measured on a monolayer film processed at pilot scale.

The previous results show us that PE/EVOH looks like being less impacted by the introduction of recycled materials than PE/PA or PE/PET blends. It is surprising that PE/PET does not impact more the properties of the film or the stability of the process considering the viscosity behaviour of the blend (described in previous chapter) so further study should be considered in term of gel counting and process stability at different concentration. PE/PA blend also shows differences between post industrial wastes (no or low impact on mechanical properties) compared with the household waste reprocessing. This could be explained by the ageing of the household waste and also by the presence of different polyamide (6, 6/6,6, …) in these films while there is only polyamide 6/6,6 in the post-industrial waste.

Guidelines

The studies previously described allowed us to demonstrate, first of all, that PET/PE blends, even if it showed astonishing results after upgrading, are the most difficult ones to recycle and reprocess because of its too different viscoelastic behavior and its needs to be processed at high temperature. The preferred path for this stream will surely be physical recycling but there are no ways to ensure that there will not be any PA or EVOH layer that would create big difficulties in this process. Considering these points, we consider that PET should be avoided in any flexible structure, would it be for packaging or agricultural purposes.

Considering the metalized fraction of the flexible waste, the biggest issue is the sorting as it disturbs the analysis of the NIR spectra. Still, as these structures are very difficult to replace today and as we show that physical recycling of a mixed metalized material is possible, we think that metalized flexible polymers should be authorized only if they are not combined with polar layers or surfaces that risks causing gelation of the solvent in physical recycling. Moreover, to allow better efficiency and higher output of this process, metalized PET should also be limited as the PET fraction cannot be recovered in this process (would need a second step).

For the PE/PA, many differences were pointed out according to the different material present in the recycled films. PE/PA could give good properties (puncture -> TD resistance) and could, according to the results of industrial scale trials with real wastes, follow a path of upcycling using innovative technologies studied in CIMPA. The next challenge would be to be able to sort recyclable PE/PA (copolymers 6/66) from non-recyclable PE/PA. Further studies should be conducted to determine exactly the polyamides that give good result when recycled with PE and the ones that degrade the final properties.

The PE/EVOH multilayer is actually not sortable using NIR technologies but might be so if using new tracing technologies such as CurvCodes. Still, as demonstrated at industrial scale, even at high concentration of rPE/EVOH the final films still show good properties, so for us this material should keep on being recycled with actual PE stream that even dilutes more the EVOH in the PE.

Finally, as a common guideline, CIMPA consortium also demonstrated the necessity to use compatibilizer when mixing different material. Indeed, we showed that adding a maleic anhydride grafted polymer in PE/PA or PE/EVOH blends allows to improve the properties of the final product. As the base resin of this compatibilizer does not impact the final properties, this polymer should be the same as the one representing the main part of the film (PE or PP). Further studies should be considered for the compatibilization of PE/PP blends and on the recyclability of polypropylene in polyethylene and vice versa even if the physically recycled rPO tends to show that PE/PP blends are recyclable.

If a PE/EVOH or a PE/PA stream had to exist (post industrial waste, separation via Curvcode, …), further study should be conducted with new technologies studied in CIMPA (METEOR or MNL) to create a added value recycled material that could bring higher properties to the film and allow diminution of thickness or lower use of high cost material (replacement of tie layer by PE/EVOH blend, better impact resistance with PE/PA blends).

Based on these studies, the guidelines for design that address this report are the following ones:

1. As long as it is possible, flexible packaging or agricultural film should always be designed as a mono-material, PE or PP for food packaging, only PE for agricultural films.
2. If barrier and/or particular thermal properties are necessary it should be addressed by one or more EVOH layer(s) that consist in less than 5% by weight rate of the final structure as long as there is at least 1.5 times the quantity of EVOH in the structure that is a tie layer and that a compatibilizer is added (further studies needed on the concentration of such compatibilizer).

3. If thermo-mechanical properties cannot be achieved using the aforementioned solutions (2) it is recommended to use one or more layer of PP consisting in less than 20% by weight of the structure with a compatibilizer (type and quantity of compatibilizer to be studied)
4. If the mechanical properties cannot be achieved using the aforementioned solution (2-3) it is recommended to use one or more layer of PA 6/66 that consist in less than 15% (further studies should assess this number) of the final structure as long as there is at least 1.5 times the quantity of PA in the structure that is a compatibilizer or tie layer.
5. If barrier properties (water vapor barrier particularly) cannot be achieved, then the structure should be realized using a complex of metallized polyolefins that do not contain the metal layer on the outer side of the packaging, no other polar material should be added as EVOH, PA or varnishes when considering this solution.

Moreover, as regard of sustainability, the project should also consider guidelines about the use of recycled material:

1. For common applications, when no particular properties are needed, PE or PE containing less than 5% EVOH recycled material should be used.
2. If high mechanical properties are needed, PE containing less than 15% PA recycled material should be used.
3. For applications where high purity recycled material is needed, a PO recycled grade from physical recycling should be used.
4. No recycled material containing other materials than PE should be used with a third material (for example R-PE/EVOH should not be used in a structure with PA).

New designs

Considering these guidelines, new designs have been established that were used as use cases in the demonstration phase. The first one will be the demonstrator for food packaging application. This application will need oxygen barrier and should be, as much as possible, a mono material. To be able to have all the necessary properties that are:

- a sufficient differential in thermal resistance between inner and outer layer to enable a good sealing;
- good barrier properties (to oxygen and water vapor);
- good optical properties;
- no major defect that would risk to break the barrier to gas.

And to answer the need of the guidelines, the choice is to design a mono PE complex film, like an oriented PE film laminated to a barrier (EVOH) sealant film. If possible, this film should also contain some recycled material. From what has been established earlier, it could use physically recycled PE in the oriented PE film as it has good purity. It is also possible to use some PE/EVOH recycled material for the laminated layer of the sealant as this one does not need any thermal properties.

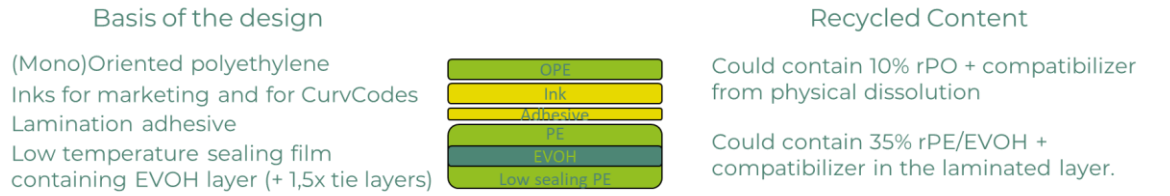


Figure 16. Design of a food packaging structure in agreement with CIMPA's guidelines.

The second design is the one of an agricultural film that should be used for silage application. This film will need to have good mechanical properties regarding the puncture and the tear resistance. It should also be stable for long term application and UV exposure.

The choice here Is to have a three-layer PE film (to keep the benefits from mono material) and have PE/PA recycled content in the core layer at least at around 50% that will make a 30% recycled content film (knowing that the core layer represents 60% of the structure).

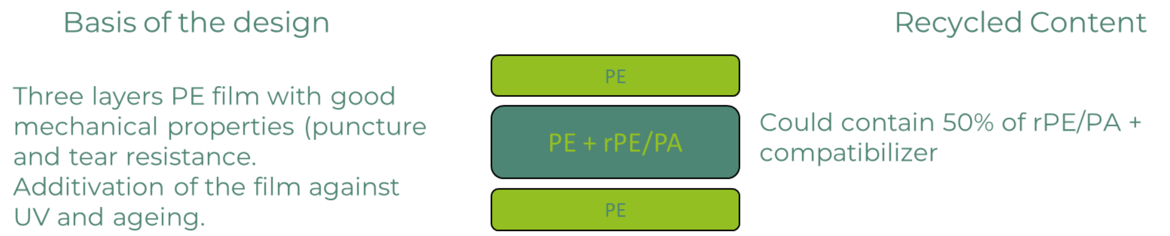


Figure 17. Design of a silage film structure in agreement with CIMPA's guidelines.

These two designs were partly demonstrated at pre-industrial scale within CIMPA project (the OPE film could not be processed due to the lack of rPO from WP4). The public deliverable D5.5 details the results of this demonstrators. For the first example one of the goals of the new technologies used in CIMPA, but only demonstrated at pilot scale, would be to obtain some barrier properties using METEOR with rPE/EVOH material or at least having an adhesion effect to reduce tie layers in the structure (keeping compatibilizers for recycling). This could lead to the reduction of EVOH layer thickness or to the replacement of layers 2 and 4 in the PE/EVOH/PE structure (cost savings). For the second design, MNL technology using rPE/PA and virgin PE could lead to a substantial reduction in thickness and maybe also give some barrier effect (useful for some applications).

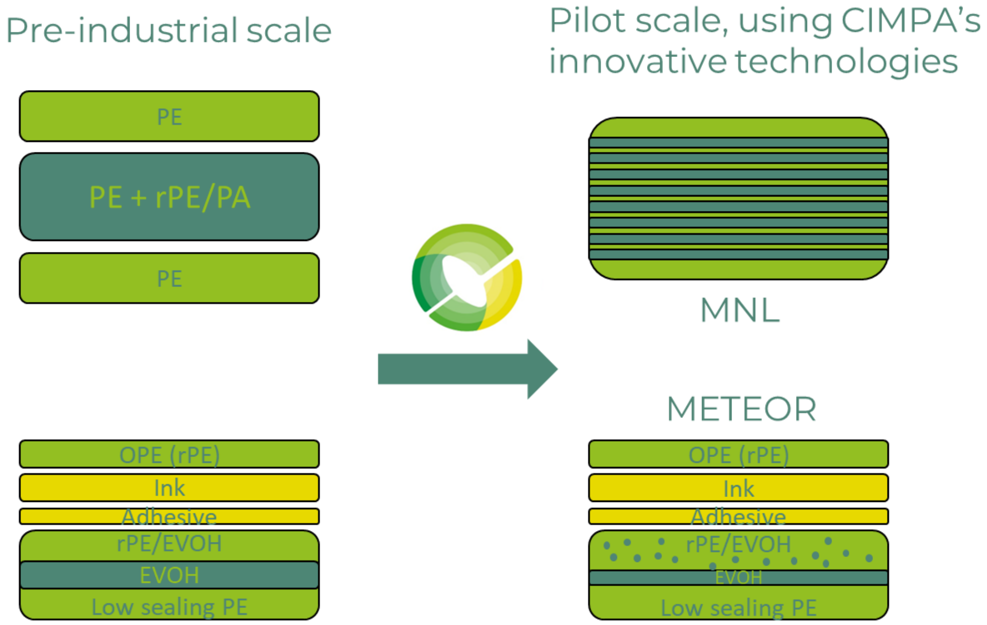


Figure 18. Possible achievement in innovative design with CIMPA technologies.

Conclusion

Today the best option when it comes to the design of a flexible plastic packaging is, definitively, the mono material structure. Nevertheless, when highly demanding properties are needed the other resins as EVOH, PP or specific PA may be used. To keep the value of this materials, particular recycling paths should be followed, and new structures will be created with sustainable secondary raw material.

The work done in CIMPA allowed the consortium to produce the two demonstrators exposed before. These two demonstrators show that it is possible to reuse recycled films in their first application (PE/EVOH/PE recycled material back in PE/EVOH/PE structure) or even in other added-value forms (PE/PA from food packaging reused to reduce thickness of agricultural films).

CIMPA studies also show the importance of compatibilizers and of the up-cycling process that allow to obtain better properties in the final product. For such reason, compatibilizer should be integrated in the structure of new films that are designed for recycling.

Finally, CIMPA partners also demonstrated that using physical recycling is a good option when highly purified material is needed (for orientation process for example) but that the films going through this process must be well designed at the basis (no EVOH, PA or other polar varnishes).

Next recommendations for further studies were also proposed and consist in:

- Studying the properties of blends made with different kinds of polyamide and polyethylene to understand which ones are really compatible with each other;
- Studying the impact of the concentration of Maleic anhydride in compatibilizers over the compatibilizing effect;
- Improving the physical recycling process with a better filtration step to allow the use of the recycled material in transparent structures;
- Improve METEOR process to be able to obtain intermediary barrier properties.