FINAL PUBLISHABLE SUMMARY REPORT

EXECUTIVE SUMMARY

The SUCCIPACK project was a 3-year European FP7 project coordinated by Actia. It aimed at investigating how polybutylene succinate (PBS) materials could answer the requirements of the food industry. SUCCIPACK considered the entire life cycle of packaging from the raw materials production to its end of life. The French company ARD (Agro Industry Research and Development) realized the first worldwide production of PBS with 100% bio-based succinic acid using wheat as a feedstock. The PBS has been formulated by Natureplast to adapt its properties for the processing of food packaging (film extrusion, thermoforming and injection molding). Films, trays and cups have been produced by Leygatech, Velfor and the CTCPA for the packaging of cheese, meat, fish and vegetarian dishes. Barrier properties of the materials have been adapted by surface treatments to each product specifications by VITO and Topchim from Belgium. Safety and quality tests realized by LNE and CTCPA proved that the new material is suitable for food packaging. This outcome was confirmed by AINIA, Vysoka Skola Chemicko-Technologicka (VSCHT) of Prague and the University of Bologna (UNIBO) by evaluating quality parameters and shelf-life of different foods (raw meat, lettuce, peanuts, cheeses, vegetarian and ready-to-eat products) provided by SMEs (Mambelli, Ortoreale, Gimar, Combio) and packaged with the innovative PBS materials.
Finally, the National Technical University of Athens (NTUA) and the BIODYMIA laboratory from the University of Lyon developed a suitable method of Solid State Polymerization (SSP) to improve PBS properties and its recycling ability. The environmental performances have been measured by 2B to optimize the different production routes of PBS and guide the material development by means of ecodesign feedback.

FINAL REPORT: SUMMARY DESCRIPTION OF PROJECT CONTEXT AND OBJECTIVES

SUCCIPACK aimed to support European industry efforts to introduce biobased polybutylene succinate (PBS) as a new material on the food packaging market.

PBS is produced with monomers obtained by bacterial fermentation: succinic acid and 1,4-butanediol that can be synthesized from succinic acid. It is a rubbery (soft) semi crystalline polymer with a glass transition temperature (Tg) around -30°C. With a melting point at 110°C, PBS can be considered as a standard thermoplastic which can be used in a large range of applications between -20 and 100°C. The cristallinity and the semi polar structure confer a good rigidity to this soft polyester. The high crystallisation rate allows high speed industrial processes, as it is the case for polypropylene. From a thermo-mechanical point of view PBS is close to polyolefins and very far from PLA. PBS is considered as a middle oxygen barrier, and a middle/poor water barrier.

The project explored the potentiality of this new material by developing adapted PBS grades, structures, formulations, treatments and recycling routes. Its environmental impact has been evaluated through Life Cycle Analysis (LCA).

The project has 5 specific objectives:

Specific objective 1: Develop new polymers, materials, and treatment technologies, optimized for different food packaging applications, allowing flexible transformation processes, and transfer the technologies to food SMEs

Special emphases on original approaches have been placed, such as:

- Material compounding and processing: special emphasis have been placed on the relation between soft polyester material composition and the transformation process flexibility, with a particular focus on film blowing
- Controlled respirability: a set of materials covering a large range of O2 and CO2 permeability has been developed through blending and copolymerization strategies.
- Material treatments: research was focus on an original barrier coating process, based on atmospheric plasma technology in combination with sol-gel chemistry.

Specific objective 2: Evaluate and improve the migration behaviour of PBS based packaging materials

The objective was to provide the basic tools for PBS evaluation, i.e. analytical procedures and data for migration prediction. The impacts of material formulation and hydrothermal history have been also studied.

Specific objective 3: Evaluate the environmental and economical benefits by considering different scenarios of material development, food packaging applications, and recycling strategies

The objective was to evaluate scenarios focusing on low environmental impact (basic packaging systems), and other scenarios focusing on food preservation (complex packaging systems), in order to access to the best routes of PBS packaging / food development.

Specific objective 4: Decrease the environmental impact linked to the production of PBS by evaluating new monomer productions from biotechnologies and by reducing the energy consumption during the polymer synthesis.

A special focus has been brought on solid state polymerization which can decrease the energy consumption associated to polymer synthesis and lead to better mechanical performances thanks to high molecular weight structure.

Specific objective 5: Improve the recycling step

Two recycling routes have been considered: material recycling for PBS standard material, and chemical recycling for complex materials.

FINAL REPORT: DESCRIPTION OF THE MAIN S&T RESULTS/FOREGROUNDS

Succinic acid and PBS production

The first goal was the investigation of the impacts of co-monomer type, chain branching, on basic polymer characteristics and on the associated packaging functionalities. This fundamental understanding of branching and co-monomer addition and how it influences polymer properties was essential for tailoring a polymeric material for high performance applications.

In this way, preliminary work at the lab scale dealt with the synthesis of branched and copolymerized PBS for film and trays applications by melt polymerization techniques. Several biobased or potentially biobased co-monomers such as diols and diacids have been tested (such as adipic acid, ethylene glycol, propanediol, furanedicarboxylic acid) in order to modulate the properties of PBS. The production of high molecular weight linear, branched and randomly copolymerized PBS have been done at the laboratory scale by melt polymerisation. Only **co-polymers with low content of co-monomer have been synthesized and tested for their thermal properties../**

The second goal was the development of a new methodology for the synthesis of PBS. In this way, innovative route based on Solid State Polymerization (SSP) have been tested. Solid state polymerization is a typical industrially applied process for step-growth polymers such as polyesters and polyamides. Accordingly, starting materials are heated to a temperature higher than the glass transition point (T_g), but lower than the melting point (T_m) with constant removal of by-products from the reaction system by passing inert gas or by maintaining reduced pressure. All reactions take place in the amorphous phase of the semicrystalline polymers, where there is sufficient segmental mobility for the end groups to diffuse and react. A number of parameters is associated to each rate controlling step, with the most important being temperature, prepolymer molecular weight, morphology and crystallinity and reactor loading. On this basis, the influence of temperature, prepolymer molecular weight, crystallinity and reactor loading, were elucidated, so as to provide an optimized SSP profile.
SSP was successfully applied in the case of PBS as a $M_w$build-up technique. A remarkable increase in terms of molecular weight for PBS oligomers was achieved when nitrogen was used as a carrier gas. Introduction of a precrystallization step prior to the main SSP process have been established in order to reduce the prepolymer melting window. **However, polymers with deficient reactive groups exhibit limited SSP performance, due to the absence of appropriate reactive groups.** This was found to be the case in a number of PBS grades, showing that the effect of SSP on the M_w improvement is limited when higher molecular weight oligomers were used. Therefore, it would be difficult to obtain macromolecules useful for material applications.
Additionally, the role of SSP technique as a crystallization/reorganization has been investigated. SSP proved to be also an effective route towards thermal properties upgrading. An increase of the melting temperature (T_m) up to 10.4 ^oC ($T_{initial}$ =113 ^oC → T_{final}=128^oC) was achieved. **Regardless of M_w variation, SSP functions as a crystallization/reorganization process, leading to upgraded end products.**

Finally, the main objective was the production of a large quantity of adapted. Synthetic routes developed at the laboratory scale were tested and used. All the PBS synthesis at the pilot scale have been done using melt polymerization techniques and using biobased succinic acid provided by BioAmber. Moreover, **two technology pathways for BioPBS production into functional polymers for packaging applications have been investigated:**

(i) **Oligomerisation/SSP post condensation**: This first pathway valorizes the flexible route based on oligomers production. The advantage is the versatility of the material which can be post modified by different methods. The second advantage could be the LCA of the whole pathway (i) compared to pathway (ii), particularly in terms of energy consumption. About 400 kg of biobased PBS have been produced for the project. However, the final characteristics of the polymer which has not all the properties required for packaging applications (molecular weight too low) cannot be sufficiently upgraded by SSP or reactive extrusion.

(ii) **Polycondensation**: This second pathway keeps the initial target of PBS production at M_w > 120000 g/mol. The advantage is to produce a directly adapted grade for different types of transformation. After synthesis and pelletization of polymers, about 45 kg of each grades of biobased PBS have been produced for the project. Moreover the characteristic of the final polymer are close to the targeted specifications.

Environmental impacts

The environmental performance of novel bio-based PBS was evaluated through Life Cycle Assessment (LCA). The aim of LCA is to quantify and assess the environmental impacts associated with a product, process or service along their whole life cycle, "from cradle to grave".
The objective of the screening LCAs carried out in the SUCCIPACK project was to **evaluate the environmental performance of bio-based PBS according to different production scenarios**. Moreover, the studies compared new solutions to establish plastic granulates used for food packaging. The goals of these LCAs were to identify environmental hotspots and to provide ecodesign feedback to the SUCCIPACK consortium. The environmental evaluation was performed with a broad set of environmental indicators, in order to offer an exhaustive analysis.

Several screening LCAs have been conducted on bio-based PBS. Scenario analyses have considered the following aspects:

- Production routes of PBS monomers: use of renewable or fossil-based resources, different production routes for succinic acid (i.e. sodium hydroxide used to neutralise succinic acid, with sodium sulphate as co-product; ammonia used to neutralise succinic acid with ammonium sulphate as co-product both with a higher and a reduced amount of ammonia; direct crystallisation of succinic acid with data from literature).
- Polymerisation process (melt polymerisation of high M PBS; melt polymerisation of low M PBS followed by solid state polymerisation).
- PBS formulations with additives (talc, PLA, PBSA, Joncryl®).
- End of life options (mechanical and enzymatic recycling, landfill, incineration).
- Surface treatment of PBS films (plasma coating).

Results show that the most critical aspect in the life cycle of bio-based PBS is the consumption of energy. In particular, the energy employed for the production of bio-based succinic acid gives the most relevant contribution, since succinic acid is used to produce both BDO and PBS. The reduction of energy consumption, especially for the production of succinic acid, should be considered as a priority in the optimisation of bio-based PBS and its technical feasibility should be evaluated.

The best results concerning synthetic routes for succinic acid production, have been obtained with direct crystallisation modelled with literature data from Cok et al. (2014)[1]. The second best production route involves a reduced use of ammonia for neutralisation of fermentation broth, which delivers ammonium sulphate as co-product.

The use of SSP to increase molecular weight of low M PBS could reduce the environmental impact of high M bio-based PBS. This alternative is not currently applied to PBS besides lab scale and therefore the environmental evaluation has been performed with estimated data referring to pilot/industrial scale. For this reason, the potential reduction of environmental impacts due to SSP might not be fully representative for the upscaled system, even though these first results are promising.

[1] Cok B., Tsiropoulos I., Roes A.L., Patel M.K. (2014). Succinic acid production derived from carbohydrates: An energy and greenhouse gas assessment of a platform chemical toward a bio-based economy. Biofuels, bioproducts & biorefining 8, 16-29.

Concerning PBS recycling, the environmental impact of recycled materials is lower than the one of virgin bio-based and fossil-based PBS both for enzymatic and mechanical recycling. Enzymatic recycling shows higher environmental impacts than mechanical recycling especially because recycled building blocks need to undergo a new polymerisation process in order to produce bio-based PBS. Nonetheless, enzymatic recycling would be particularly useful in case of PBS compounds and copolymers recycling. A large part of the environmental impacts of recycled PBS is due to the collection and pre-treatment phases. The uncertainty related to these phases is high, due to the use of background data, and recycling techniques are not currently applied to PBS besides lab scale.

Blending of PBS with additives can modify the environmental performance of the material as well. For instance, blending with talc would improve the environmental performance of bio-based PBS, whereas blending with PBSA would increase its environmental impact. The use of PLA as additive would also reduce the environmental impact of the plastic granulate for most impact categories.

Plasma pre-treatment, coating deposition and drying would increase the environmental impact of PBS film, since data on plasma coating and drying mainly refer to pilot scale. The contribution of these processes to the environmental impact of coated PBS film is expected to decrease with upscaling of the technology (industrial scale), even though this reduction cannot be quantified at present.

The environmental performance of bio-based PBS was compared to established plastic granulates (e.g. PET, PA6, PLA) **and conventional food packaging materials of interest for the project.** Packed food products include fish, vegetarian ready meals, ready-to-eat vegetables, dairy products and raw white meat. The comparison has been conducted from cradle to grave, including end of life of plastic granulates and packaging materials, and food in the case of packed food products. Different plastic materials were compared based on their volume, assuming an equivalent function between packaging items of the same size and thickness. The aim of the comparative analysis was to provide ecodesign feedback to the SUCCIPACK consortium in order **to optimise the production process of the novel material**.

At the current state of development of bio-based PBS production technology, the use of PBS packaging would increase the environmental impacts of the food products under study. The increase of the environmental impact of packaging is more evident in case of vegetable products (vegetable couscous, grilled peppers and marinated tomatoes), whereas for animal-derived products (cheese and ricotta, chicken and fish) it is more limited, both because animal-derived products have higher impacts than vegetarian products, and because for some of these products (e.g. chicken and ricotta) the ratio mass of packaging/mass of food is low.

Currently, the environmental impacts of bio-based PBS are higher than those of some traditional plastic granulates (e.g. PET) and other bio-based plastics (e.g. PLA), whereas PA6 has higher impacts than bio-based PBS for some impact categories. Moreover, a higher amount of bio-based material is needed for the same amount of packed food due to its higher density. The increase of the environmental impact of packaging could be justified if this increase resulted in a lower rate of food waste, reducing the overall environmental impact of the packaged food product.

Whereas traditional plastics are produced through a well-established and mature technology on industrial scale, bio-based PBS is at an early stage of development, and far from full industrial scale. **The main aspect to improve the environmental performance of bio-based PBS is the synthesis of succinic acid; in particular, alternative synthetic routes could be tested**. For instance, according to literature data, succinic acid produced through low pH yeast-based fermentation followed by direct crystallization has lower environmental impacts. In general, **bio-based PBS can be an interesting material for packaging applications but its environmental performance should be further improved**.

The use of LCA in an early stage of development of new processes or products is particularly useful, providing valuable feedback for product improvement. The LCA results obtained in the project derive from screening LCA studies. Screening LCAs enable to make quick comparisons, but use a large amount of background data. The values obtained and the resulting conclusions could change if more precise data were available (e.g. realisation of pilot or industrial plants). **Furthermore, many data used in the evaluation refer to lab or pilot scale; improvement of the environmental performance of the material could be expected if the processes under study were implemented at pilot or industrial scale.**

Processing of PBS

PBS grades adapted to various processes are available on the market, with viscosities (and subsequent Melt Flow Index) adapted to standard plastic processing methods. **They are well adapted for all processes** (extrusion of foil, thermoforming and injection moulding) **but not for extrusion blowing and film production**.

PBS grades are suitable as pure materials, without equipment modifications. However some improvements may be needed depending upon processes and targeted application:

- for injection moulding : a quicker crystallization kinetics may be needed to decrease cooling time
- for thermoforming : a higher modulus at solid state and a better cohesion in the process condition may be needed
- for film blowing : bubble stability during film blowing operations has to be improved

To improve PBS processability, the following options should be advised:

Increasing crystallization rate (injection moulding)	Increasing modulus at solid state and cohesion at molten state (foil extrusion - thermoforming)	Improving bubble stability (extrusion blowing)
- blending with PLA - blending with talcum powder - blending with TPS	- blending with PLA - blending with talcum powder	- blending with PBSA - blending with PBAT

The formulation work has taken into account the need to find compromise between improving processability (increase cristallinity, ease film blowing ability, etc.) and maintaining good level of properties (brittleness vs softness). The main recommendations for PBS formulations are summarized below:

Blending PBS with	Maximum content advised	Targeted process
PLA	15 wt%	Injection moulding Thermoforming
TPS	15 wt%	Injection moulding
PBSA	25 wt%	Extrusion blowing
PBAT	15 wt%	Extrusion blowing
Talcum powder	20 wt%	Injection moulding Thermoforming

Processing guidelines have also been built depending on the nature of the polymer or compound and the process considered.

Prior to any processing, PBS and PBS-based compounds pellets should be dried 4 hours at 80°C in an oven or a desiccator except for blends with PBSA and PLA were temperature should be lowered (around 60°C).

Depending on processes, the following temperature ranges should be advised for selected PBS grades and PBS-based compounds:

Processing method	Extrusion	Foil extrusion	Thermo forming	Injection moulding	Extrusion blowing
Material or blends	All except with PLA	PBS PBS-talcum	PBS PBS-talcum	PBS PBS-talcum PBS-TPS	PBS PBS-PBSA PBS-PBAT
Temperature range	110-130°C	110-130°C	105-115°C	130-150°C	Not suitable
Comments	Cooling in water Standard pelletizing		Foil thickness >300 µm for PBS	Mould at ambient temperature	

Higher temperatures may be used, up to ~200°C, however degradation and chain scissions may occur if residence time at those temperatures is not kept low (increase in fluidity and loss in properties are observed).

For blends with PLA, due to the higher melting temperature of PLA, processing temperatures have to be increased. The following ranges should be advised, in case PLA amount remains lower than 15 wt%:

Processing method	Extrusion	Foil extrusion	Thermo forming	Injection moulding	Extrusion blowing
Type of blends	PBS-PLA	PBS-PLA	PBS-PLA	PBS-PLA	PBS-PLA
Temperature range	160-170°C	160-170°C	110-120°C	160-170°C	Not suitable
Comments	Cooling in water Standard pelletizing			Mould at ambient temperature	

PBS is not compatible with a wide variety of polymers. An extended purge of the system might be considered.

In a nutshell, except the need of special grades for extrusion film blowing, the improvement of the material properties can be obtained through available commercial grades associated to different compounding strategies, by blending PBS and its copolymers with other aliphatic polyesters or with mineral fillers.
Guidelines for smart processing are proposed in Deliverable D.2.7.

Properties of PBS

Barrier properties

PBS shows an intermediate behaviour between breathing polymers (showing both high water and oxygen permeability) and barrier polymers (showing both low water and oxygen permeability) such as PET and PEN.
Compared to PP, PBS is a lower water barrier but a much better oxygen barrier.
Compared to PLA, PBS is a PBS has better oxygen and water barrier properties. This is attributed to its crystallinity.

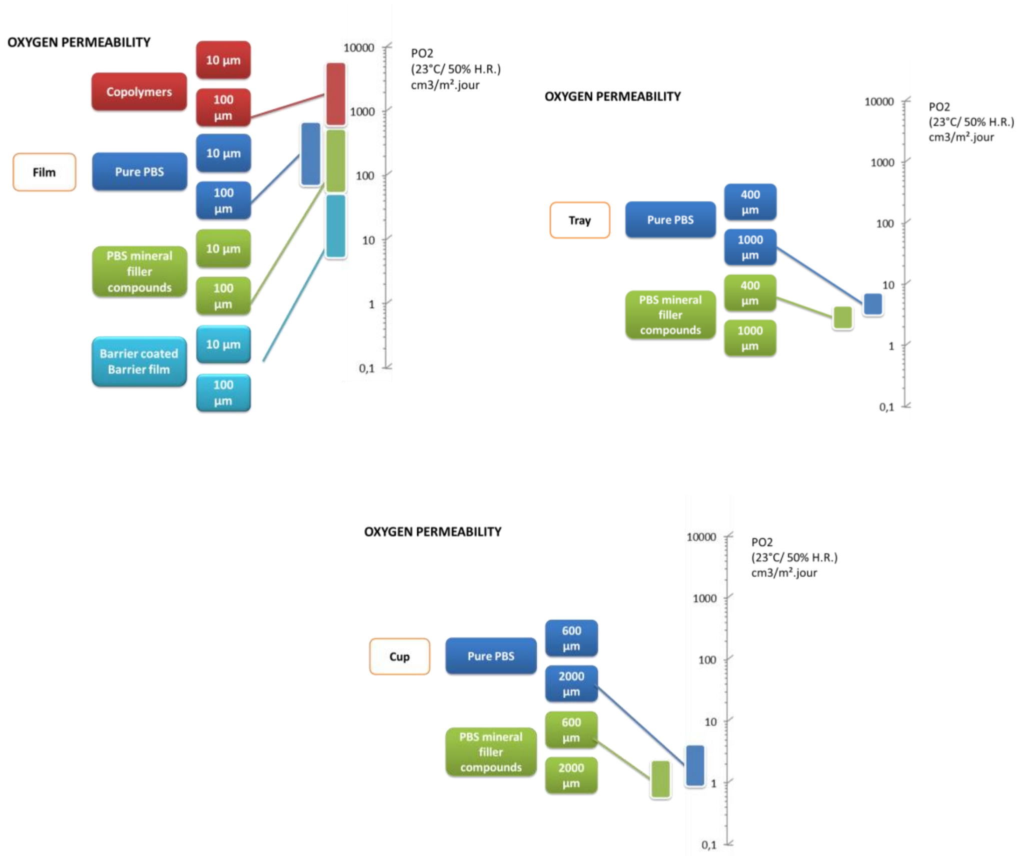
Different materials have been studied, in order to establish the possibility to **modulate permeation properties through the formulation and through the polymer modification by copolymerization.**
Concerning the water permeability of PBS based materials, a factor 4 is observed between the (high) permeability of PBAT and the (low) permeability of Talc filled PBS.
Concerning the oxygen permeability of PBS based materials, a factor 10 is observed between the lowest permeability of PBAT and the highest permeability of Talc filled PBS.

The **improvement of barrier properties by the use of SiOx coating** has been studied on different substrates and successfully on PBSA. A factor 10 is observed for the improvement of oxygen barrier properties while a factor 7 is observed for the improvement of water barrier properties.

The improvement of barrier properties by hydrogenated carbon (**CxHy)** plasma treatment was studied by the 3D coating of PBS injected cups; no improvement was obtained, confirming that the plasma treatment (SiOx or hydrogenated carbon) of <u>pure</u> PBS is technically difficult.

The improvement of permeability was then studied by green water based coatings. Two kinds of green water based coating were tested: TopScreen 30A1 (TopBrane) is a coating formulation that Topchim has developed to ensure a good oxygen barrier on flexible packaging. The transparent coating contains an immobilizer, polar pigments and a polar polymer. TopScreen DS3V is a coating formulation that Topchim has developed to ensure a good water vapour transmission barrier on flexible packaging. The transparent apolar coating contains a lamellar structured pigment with high aspect ratio.
With Topscreen DS3V a factor 4 was observed for the improvement of oxygen barrier properties while a factor 2 was observed for the improvement of water barrier properties. With the Topbrane coating, only water permeability is improved (factor 2)
The combination of the two types of coating leads to a good reduction of both oxygen and water permeability. Due to high water sensitivity, the oxygen barrier must be applied in the external part of the packaging to avoid migration issues and damage of the coating. The best combination of the coatings is then obtained with the oxygen barrier deposited on the external side of the packaging, and the water barrier on the internal side.

The improvement of permeability was finally studied by the modulation of packaging type and thickness. The permeability of a material is strictly inversely proportional to the sample thickness when the material structure does not vary with the thickness: barrier properties of films and thermoformed trays vary with the polymer orientation; concerning injected packaging the permeability varies with the crystallinity of the material. As a consequence, the change of the types of packaging leads to sensible variations of Pe/l (l sample thickness). **Permeation charts were built to select, from targeted water or oxygen permeability, the best PBS based packaging. The example below concerns the oxygen barrier properties.**



Oxygen permeability of films cups and trays

In a nutshell, a very large range of permeability can be accessed thanks to the types of formulation and sample thickness. The best flexibility is obtained with the films, with 3 decades of possible oxygen permeability.

Breathing properties

The permeability analysis permitted to measure the CO_2 transfer and its selectivity compared to oxygen. A factor 7 was observed from the lowest CO_2 permeability of PBAT and the CO_2 permeability of Talc filled PBS. The ratio between CO_2 and O_2 permeability (also called the selectivity) varies from 10 for PBAT to 14 for PBS and PBS compounds. These values are higher than the common reported values in literature for classical packaging materials (from 3 to 6). This high selectivity of all PBS based materials is of a great interest for the packaging of fresh food products which are better preserved in conditions of slow oxygen penetration and fast CO_2 release.

Materials that present selectivity for the CO_2 permeability are especially useful for packaging products that generate CO_2 during their storage, like ripened cheese, or fresh vegetables, among others. In particular, fresh vegetables continue breathing during their storage. Thus, in order to extend their shelf-life it is necessary to reduce the breathing rate of the product for reducing its biochemical activity, which implies to select the proper modified atmosphere, and film for the packaging.

For the practical tests fresh-cut lettuce has been selected as product, and compared to the commercial packaging film with 3 kinds of PBS based films: PBS (20 μm), PBS (30 μm) and a PBSA/PBS film. For the comparison tests, microbiological parameters selected were *Listeria* spp. and the level of mesophilic aerobic microorganisms.

The results showed that the level of *Listeria* spp. remained the same for samples packed with the commercial film and with all the PBS based films. Concerning the level of mesophilic aerobic bacteria the tests showed, in general, a lower level of microorganisms for the products packed with the PBS based materials.

Mechanical properties

As already underlined, there is a limited choice in commercially available PBS grades. This means that pure materials cover a small range in mechanical properties, while PBS may be used for various packaging applications with different flexibility (from flexible for film applications to rigid for trays applications).

Standard PBS grades exhibit mechanical properties similar to polypropylene (PP) and high density polyethylene (hdPE):

- Young's modulus of about 0.9 GPa
- Flexural modulus of about 0.6 GPa
- Stress at yield of about 40 MPa
- Elongation at yield of about 10%

Mechanical properties of PBS can however be modified by various compounding routes. Among others, blending and additivation can be used to modify properties. PBS then behaves as a standard polymer, with properties varying with the intrinsic properties of the added component, and its mass proportion inside the blend. Modulus as an example can so be increased up by 100%, or be decreased in the same proportion.

PBS mechanical properties can be adapted to various books of specifications for packaging applications. While keeping the food contact aptitude of pure PBS, the following blends may be advised, in line with the blends advised to improve processability:

- **Flexible packaging (film application): PBS + PBSA/PBAT**
- **Rigid application (trays, thermoforming application): PBS + PLA/talcum powder**

Packaging applications using injection moulding: PBS, PBS + PLA/talcum powder for rigid packaging, PBS + PBSA/PBAT for flexible packaging. In each case, the amount of the added component has to be adapted to the needed modification extent.

Thermal properties

The review of the thermal characteristics of all PBS polymers produced in SUCCIPACK highlighted that the **melting points (T_m) ranged from 109 to 115 ^oC**, with the lowest values documented in the case of bio-based PBS grades (bPBS). Fossil-based PBS grades (fPBS) proved to be more homogenous compared to bPBS grades, as indicated by their sharper melting endotherms and their practically negligible melting point deviation (fPBS: stdev ~ 0.1^{o}C/ bPBS: stdev ~ 2.9 ^{o}C).

Therefore, the development of techniques towards increasing PBS melting point and/or homogenizing material thermal properties emerged during the project as an important issue to be considered for the range of polymer application and commercialization. To this direction, solid state polymerization/treatment (SSP/SST), i.e. heating the material at appropriate temperature between T_g and T_m in inert atmosphere, turned to be a valuable tool towards repairing any thermal stability issues and thus upgrading polyester quality.

In particular, for all PBS grades studied in the project – fossil and bio-based- **SSP served as a post-crystallization method**, improving the lamellae morphology by forming more stable and perfect crystals, and in parallel eliminating any metastable/imperfect species of lower melting points. As a result, sharpening of the melting endotherm and increase of the melting point were documented during PBS SSP/SST, **reaching an upper limit of ca. 124^{o}C and accompanied in most cases by crystallinity increase**.

This improvement of PBS thermal properties occurred regardless of the molecular weight build-up in the course of the SSP process and this feature is extremely useful in case of bio-based material, where the potential presence of bio-based succinic acid impurities maybe problematic for the quality of the material. In a nutshell, **SSP represents a useful tool with great potential in the industry towards improving PBS thermal properties**.

Other strategies of copolymerization with rigid acid monomers were also tested to increase the melting point of PBS. No improvement was obtained.

Food contact properties

The requirements of European regulations in the field of food safety are the following:

- Basic components of the material are to be included in the positive list
- Substances with restrictions must be controlled (specific migration in intended conditions of use must be lower than specific migration limits) either by experimental tests, or with migration modelling
- The overall migration must be less than 10mg /dm^2 packaging

- The contact between the packaging and the food must not cause changes in product organoleptic characteristics
- Non intended added substances must be identified and further evaluation is needed for eventual critical substances

Basic components
Succinic acid and butanediol1-4 are in the positive list identified as monomers; PBS which results from the polycondensation of both building blocks meets the polymer composition requirements of regulation EU 10/2011 on plastic materials and food contact materials.

Experimental specific migration tests
As no restricted substances were used in the formulation of PBS in the SUCCIPACK project, no specific migration test was carried out; generally PBS does not need any low molecular weight substance addition to adapt its properties which are rather adapted by strategies of polymer blending or mineral filler addition.
The virtual situation of specific migration of restricted substances was studied by the approach of migration modelling.

Modelling of specific migration
The modelling of specific migration requires the use of simple diffusion models, which takes into account (i) a Fickian diffusion in the bulk material described by a constant diffusion coefficient D (ii) a partition at packaging food interface described by a partition coefficient K. The key issue is to have the adapted mathematical tool for the prediction of D. The most often model used for the prediction of D is the Piringer model. The parameters measured ***for pure PBS*** in the project are shown in the table below.

τ	Ap'*
-827	4.5

Piringer equation parameters for PBS homopolymer

In the case of ***soft copolymers such as PBSA,*** the Piringer equation parameters of polypropylene could be used for the migration modelling (low migrant barrier properties of copolymers).

Sensory analysis
The sensory analyses were performed according to the ISO 13302 standard and Robinson test.
According to the results of sensory analysis with water, only the IBIOPBS gives an average score different from 0. In this case, it can lead to a modification of the flavour of the water by this material because the average score is greater than 1 (average=3.8).
From the results of sensory analysis with chocolate, for all samples, no significant change in the flavour of chocolate has been noted. The average score for all materials including the IBIOPBS is between 0 and 0.2.
These results generally show the influence of the type of food in contact with the material PBS. Indeed, the modification of the flavour is more pronounced for the IBIOPBS in the case of water.

Rather than attributing the defaults to the green origin of bioPBS, the sensory effect of this material was attributed to a higher monomer / oligomer content due to a higher sensitivity to hydrolysis.

Overall migration

The determination of overall migration of PBS packaging has been mainly studied on the basis of the use of ethanol water mixture food simulants.

Indeed other attempts of overall migration testing have led to severe issues:

- Migration in olive oil: to determine the migrant mass loss of a packaging after contact with olive oil, the normalized test proposes a procedure allowing to subtract the sorption of oil in the packaging to the packaging weight variation. This procedure works for most of packaging on the market but with PBS we observed a high oil sorption in the material; moreover the extraction procedure, even by modulating the time and the solvent type for the soxhlet extraction, was not efficient: the re-extraction of absorbed oil was not complete, leading to negative overall migration values. This issue was attributed both to the high level of oil sorption, and to a possible reactivity or high oil interaction with the material;
- Extraction by isooctane: this solvent preconized as substituting medium for fatty food simulant was observed as too aggressive (partial solubilisation and physical damage of all types of packaging).

The best way to access to the migration behavior of PBS was then to study ethanol water mixtures.

- Migration increases systematically with the ethanol content, as lipophilic contact increases probably both (i) the affinity of PBS oligomers to the food simulant (partition effect), (ii) and the diffusion coefficient by a plasticization effect.
- No effect of the acidity of food simulant was observed. This can be explained by a too short contact time (10 days) to induce PBS degradation. In shelf life conditions this could be an influencing factor (catalysis of PBS degradation for long contact time)
- The sensitivity to hydrolysis has a clear incidence on overall migration: higher migration was obtained on bioPBS or on samples stored more than 1 year in ambient humidity/temperature conditions.
- PBS PLA blends shows a reduced migration. During injection, a fraction of PLA migrates at the surface; PLA confers a functional barrier effect.
- Temperature and material thickness have classical effect on migration: migration at 40°C (simulating room temperature uses) can be higher than the regulation limit for thick PBS samples; at the contrary, migration at 20°C of thin PBS films is always under the regulation limit.

NIAS Screening

The identification of the migrants from different PBS packaging material was systematically studied. This approach allowed the determination of products systematically observed in PBS materials. These substances were classified in 3 families:

- Simple degradation reactions and recombinations from PBS oligomers and or from its monomers;

- Additional mechanisms leading, from the previous compounds, to cyclic compounds;
- Additives.

All these products (aliphatic esters and ethers, and common additives) are assumed not to be critical.
At the contrary some of the other compounds observed could be of potential critical structures (to be studied by toxicological tests); but none of them are observed systematically (from one type of sample to another). This shows that none of them can be considered as a systematic NIAS of PBS. Their presence is probably due to process or environmental pollution.

As a conclusion PBS materials have **no critical NIAS**. But real commercial formulation must be controlled; to differentiate the classical and anomalous NIAS, a specific annex was produced, giving the reference mass spectra of systematic NIAS.
Complete guidelines for migration testing are proposed in deliverable D3.5.

Susceptibility to hydrolysis

As PBS is an aliphatic polyester, its sensitivity to hydrolyze during both processing (degradation) or storage (ageing) was studied.

The ageing of polyester usually leads to chain scission reactions through ester bond hydrolysis, giving new molecular weight distributions as well as modification of the content of end-chain groups. Such modifications depend on the hydrolysis yield which is responsible of i) lower mechanical performances ii) low modifications in thermal properties iii) modifications in PBS polarity (OH and COOH groups increase) which can promote (if the hydrolysis level is high) a higher water hydration rate iiii) higher overall migration level due to *in situ* oligomer production. The following aspects were thus studied during the project:

- Ageing during storage: analysis performed on different lots of PBS stored at 20°C and different relative humidities showed that PBS is sensitive to hydrolysis and should be stored in dry conditions.
- Accelerated controlled ageing: PBS has been aged in different conditions of temperature and humidity. The results were used to establish a kinetic model, and can also be used as references for experimental procedures of accelerated ageing tests
- Ageing and migration: Overall migration has been performed following the CE 10/2011 regulation. The authorized limit (10mg/Kg) was systematically surpassed for trays and cups but acceptable for thin films as predictable. Oligomers as well as free succinic acids by ageing can be responsible of such results, migration tests being performed on already aged samples.

Concerning the ageing during storage, a complete quality approach has been proposed in deliverable D2.7 and the main key points are presented in the hereafter.

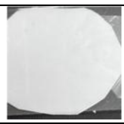
Modelling of ageing and consequences on industrial practices: A simple kinetic model was tested in the project. The decrease of M_W was assumed to follow equation 1:

$Ln (M_w / M_w0) = - k t$ (equation 1)	- M_w0 the initial M_w - t the degradation time - k the degradation rate constant
k is assumed to be proportional to (i) the water concentration in the material (ii) the initial acidic index (catalysis effect of acid end chains); (iii) a temperature activation factor (Arrhenius type).	

By measuring the degradation kinetics in different conditions of water content, initial acidic index, and degradation temperature, the model was validated for PBS homopolymer. To reduce the degradation rate of PBS materials, it was also necessary to minimize the initial acidic index, the water content all along the supply chain, and time /temperature effects.

Measurement of water content: PBS pellets have to be dried and stored in water barrier packagings. Before being processed, PBS should be dried (like PET) in an air dryer (fed with previously dried air). As quality control (for PBS acceptance lots) should be the water content determination by ISO 15512:2008.

Degradation state / smart color test: a simple color test can be made following the protocol established during this project: *PBS samples (taken in the center of the bag) are doped with CCVJ probe (CAS 72301, sigma) using a ratio probe/PBS of 100 ppm (by weight). 5 mg of CCVJ is previously dissolved in 100 mL of dichloromethane (CH_2Cl_2)* to obtain a stock solution at 0.05 mg/mL. *From this stock solution, 2 mL were added to 1 g of PBS. The mixture (probe + PBS) is dissolved in 6 mL of CH_2Cl_2 at room temperature 12 hours. A polymer film is then prepared by casting (until CH_2Cl_2 remove). If a yellow color (see below) is obtained, the lot should be rejected as the molecular weight is representative of an aged PBS sample or SSP /reprocessing have to be envisaged.*

	New PBS	Aged PBS
Doped film with CCVJ (100ppm by weight)		

Degradation state / classical tests - Degradation is associated to the decrease of M_w, and the formation of new end chains which can be characterized controlling the COOH concentration. Consequently degradation can be controlled by the evolution of acidic index, the viscosity in solution or even a SEC analysis.

Associate an accelerated ageing test to migration test?
The hydrolysis of PBS during time leads to the generation of oligomers which are the main components of the migrate. Consequently overall migration increases with ageing time, and the kinetics of migration differs from classical behaviour:

Classical migration kinetic decrease as a function of time, following roughly a linear uptake as a function of the square root of time ; the migration during 10 days is only 2 times less than the migration during 100 days. Consequently, taking into account thermal activation effects, the migration 10 days at 40°C is representative of the migration during a long contact time at 20°C. On the basis on these considerations are defined the regulation migration tests of R10-2011.

At the contrary, if new migration species are generated during contact, the kinetics will be more complex, and consequently no extrapolation will be possible from the behaviour of the unaged material.

Consequently it is suggested to evaluate the migration of both the unaged (as suggested by the EU regulation) and the aged material:

- Classical evaluation of the packaging material after processing.
- Second migration test after artificial aging of the packaging. This artificial aging should cover the worst case period of storage condition of the packaging before food contact and half time of the shelf life food contact conditions.

Aroma scalping properties

Showing a medium Hildebrand solubility parameter, PBS can theoretically interact with a lot of organic compounds. As a consequence, PBS is predicted to show a potential of high aroma scalping. Moreover due to a low glass transition, the transfer dynamics are supposed to be fast, with a potential effect of quick losses of food organoleptic properties.

As representatives of different characteristics of aroma components, the following compounds were selected to simulate wide range of physico-chemical properties: ethyl acetate, ethyl butyrate, ethyl caproate, hexan-1-ol, heptanal, R-(+)-limonene. Low density polyethylene was taken as a reference of packaging polymer with high aroma scalping properties

Aroma scalping: The permeabilities cohere well with the available literature data (ethyl acetate-LDPE [Polym. Eng. Sci. 23, 1984, 734]). The obtained results show that the PBS-based films have comparable barrier properties, i.e. permeability, as the LDPE film for polar compounds (ethyl acetate, ethyl butyrate, hexan-1-ol). On the contrary, the permeability of the PBS-based films for the less polar compounds (ethyl hexanoate and heptanal) is by one order of magnitude lower than those of the LDPE film. The permeability of the PBS-based films for the non-polar compounds (R-(+)-Limonene) is by two orders of magnitude lower than that of the LDPE film.
To summarize the results obtained by the microgravimetric measurements, the **PBS-based films have comparable barrier properties as LDPE films for polar aroma compounds** (alcohols, esters with short aliphatic chains up to C4) **and significantly better barrier properties for compounds of low polarity** (aldehydes, esters of longer aliphatic chains than C6, hydrocarbons).

Transfer dynamics: Overall evaluation of measured results shows different characteristics especially for the group of PBS based materials and PE based foil as a reference material. Depending on the differences of solubility (S) and differences in diffusivity (D) differences can be observed on the resulting permeability (DXS). Some aroma are better lost by BPS materials and others are better lost by polyethylene. For data measured by HS-SPME/GC-TOFMS the significant drop (approx. 50% for 24h) of concentrations of all tested compounds in all packaging materials was observed. Therefore the worse protection to losses of this kind of compounds in spectrum of volatiles during the storage period of packaged food can be assumed.

However, despite the observed differences, the behaviour of PBS and LDPE films with respect to the model aroma compounds was generally very close. PBS can then be classed at the level of LDPE for its aroma sorption and transfer properties.

Effect of PBS packaging on food shelf life

One of the aims of the SUCCIPACK project was the evaluation of the performances of the novel packaging materials in maintaining quality and safety of selected food products as **no or little information is actually available in literature**. In fact no papers reporting experimental results on the use of PBS packaging for food application has been recently published.

This objective was achieved through **systematic tests on several products representative of different food categories**, processing technologies and storage conditions, which in turn have different requirements in terms of preservation. In particular, the following products characterised by short and medium shelf-life values have been taken into consideration:

- Raw and smoked poultry meat packed under vacuum;
- Raw beef meat packed in air;
- Heat treated vegetarian burgers packed in air;
- Grilled peppers packed in air;
- Ricotta cheese packed in air;
- Minimally processed lettuce packed with MAP;
- Roasted peanuts packed under modified atmosphere.

As a result, successful PBS materials and conditions have been found for all the selected foods, and the applicability of the innovative packaging under the form of trays, cups or pouches has been proved.

In general the PBS materials produced within the project were characterised by the same efficiency in preserving food quality and safety as the reference ones. This is the case of the 2 PBS films used to pack under vacuum raw chicken and turkey meat as well as smoked turkey meat, which are quite highly perishable products mainly due to levels of nutrients available, high pH and Aw values. In facts, thanks to the appropriate thickness, good barrier properties towards gases and vapour, all the 3 meat products were stable and no changes in the chemico-physical and colour were observed compared to the reference (PA/PE) film. Also for the spoilage microflora, no significant differences could be detected between samples packed with the conventional film and the PBS ones thus resulting in the same shelf-life values, i.e. 5 days for raw poultry and turkey breast, and 15 days for smoked meat.

PBS films suitable for the storage of heat treated vegetarian burgers and grilled peppers were also produced. In fact, their use in the form of pouches (for the burgers) or as topfilm for bioPBS cups (for grilled peppers) allowed to protect the food from undesirable chemical/enzymatic reactions that lead to discoloration and change in flavor, odour, consistency. Moreover, the growth of the contaminating microflora responsible for food spoilage was prevented over 50 days of refrigerated storage for grilled peppers and up to 60 days for spinach burgers, i.e. 15 days beyond the shelf-life actually given by the producers to this food.

A targeted application of PBS films was achieved also for minimally processed lettuce by playing on the barrier properties of 3 different films. In fact their use as pouches for ready-to-eat salad was successful in delaying and limiting the growth of the spoilage mesophilic microbiota. This effect contributed to an increase in the lettuce shelf-life compared to the conventional packaging (BOPP).

The barrier properties of 2 bilayer PBS films were also exploited for roasted peanuts. While this product does not present microbiological concerns, one of the main factors affecting its quality is lipid oxidation, which not only influences sensory and nutritional quality of foods, but also impacts the food product's shelf-life. On the other hand, both the PBS films developed for this application were characterised by a higher barrier against oxygen compared to the control one (PET), thus limiting quality loss for this type of product.

Unlike peanuts, ricotta cheese has a limited shelf-life (~ 10 days) due to its low salt concentration, high water activity and pH values which make it highly susceptible to microbial spoilage. Since no preservative or MAP is used, its stability simply relies on Good Manufacturing Practices, chilled storage and proper packaging materials and conditions able to retard microbial growth. Therefore, several PBS materials were tested in the form of trays, cups and pouches used alone or in combination in order to find an application able to preserve the shelf-life compared to the control packaging (PP).
Overall, none of the tested PBS materials and packaging conditions significantly influenced the main chemico-physical and quality parameters monitored for this product compared to the control packaging. In fact pH and Aw values were almost stable over storage, while main changes observed for the colour, which tented to a shift to yellowness during storage, followed the same trend in the PBS-packed samples and in the control ones.
On the other hand, different behaviours were observed for the microbiota of ricotta in relation to various PBS materials and packaging combinations developed. In general lactic acid bacteria, enterobacteria and yeasts showed limited growth extents, while aerobic mesophilic and psychrophilic ones reached maximum values of 7 Log CFU/g which is the critical threshold level for the product quality. Therefore these 2 microbial groups were responsible for spoilage of ricotta cheese, i.e. for the definition of its shelf-life. Taking into consideration that oxygen in the headspace of packages is one of the main factors affecting food spoilage, as it is required by mesophiles and psycrophiles for their growth, films with good barrier properties were produced. When employed for pouches, such PBS films ensured shelf-life values comparable to the reference packaging. By enhancing their barrier properties with a surface coating their use in combination with bioPBS cups resulted in a significant extension (2-3 days) of ricotta shelf-life compared to the reference packaging. On the other hand also the composition of the material in direct contact with the food proved to affect microbial spoilage. In fact PBS cups with specific formulations were effective in delaying spoilage processes and preserving food quality, thus acting as a sort of antimicrobial packaging which allowed to achieve a 3 days longer shelf-life compared to the control packaging.

Overall, **results collected showed that several PBS-materials produced in the frame of the SUCCIPACK project have good potential for packaging applications in the food industry**. In fact PBS materials performing in a similar way as the conventional packaging were successfully developed for all the tested foods, which represent a rather wide range of products with differentiated requirements in terms of preservation. Moreover, **enhanced shelf-life was achieved** by acting on PBS formulation or improving its barrier properties, thus indicating that further applications (e.g. MAP, active packaging...) can be investigated and exploited in the future for other more or less perishable products like raw meat, minimally processed vegetables, fruit salads, bakery products….

Recyclability of PBS

In the production of sustainable and cost-effective materials, both fossil-and bio-based plastics are involved. Thus, the growing utilization of bioplastics and biocomposites has given rise to the necessity of developing an effective recycling technology for bio-based materials. Up to now, **the number of publications in open literature investigating the recyclability of PBS is limited.** Towards establishing a sustainable PBS plastic packaging, in the frame of the project the recyclability of the polyester was studied in detail, since up to now there are no specific guidelines concerning the end life of PBS.

To this direction, three recycling routes were investigated in the SUCCIPAK project, and the overall outcome was the development of the appropriate approach depending on the extent of degradation, from which the waste material suffers:

i) The remelting-restabilization approach in the concept of mechanical recycling
ii) The SSP repairing approach
iii) The oligomerization/monomerization approach in the concept of chemical/feedstock recycling

In particular, the **remelting-restabilization** route was examined, aspiring to be applied for PBS waste of low degradation extent, i.e. on PBS waste with a negligible molecular weight decrease due to usage and disposal. This route involves the addition of re-viving additives (restabilization) in order to protect the material waste when reprocessed during mechanical recycling. During reprocessing at elevated temperatures, PBS of different usage environments was found to undergo mainly a chain branching degradation mechanism. In order to restrict the formation of branches, typical primary and secondary commercial antioxidants were incorporated in PBS at different concentrations, showing that the addition of IRGAFOS® 168 and/or IRGANOX® 1010 limited strikingly PBS thermo-mechanical degradation. As a result, the remelting-restabilization approach was proven to have potential for PBS recycling, a fact which was also supported by the herein conducted LCA and LCC studies indicating the lower environmental impact of restabilized/recycled PBS compared to virgin material.

In cases of noticeable polymer degradation extent, i.e. assessable molecular weight decrease, a **recycling route based on solid state polymerization (SSP)** was suggested. This is especially the case for materials after prolonged storage at environments of increased temperature and humidity. The general concept of this technique was to submit the aged PBS to the SSP process: project runs on aged PBS grades involved heating the material in an inert atmosphere {e.g. 11 $m^3/(kg_{polymer}h)N_2$} at a temperature in the vicinity of the polyester melting point (e.g. T_m-T = 3 ^oC). Under these conditions, recovery of the molecular weight to its initial values and significant increment of the polyester T_m, even up to 10 ^oC, were observed.

Finally, in case of highly degraded PBS the route of **monomerization** is recommended. To this direction the degraded PBS is subjected to extrusion, in the presence of enzymes and breaks into its original monomers. This approach is very effective in terms of monomer recovery; however the high cost of the enzyme may limit its application in the industry.

In conclusion, (i) The extrusion process showed a significant effect on PBS depolymerization. A higher oligomerization rate was reached by twin screw extruder. This result can be explained by the higher homogenization of the (PBS + lipase) mixture which permitted a good substrate-enzyme contact. The high decrease in M_W and Mn confirms the random PBS chain scissions by lipase.
(ii) The addition of the proposed restabilization system (0.1 wt% Irganox 1010) results in satisfactory retention of the physical, thermal and rheological characteristics of the recyclates subjected up to 5 extrusion cycles.
(iii) Regarding the utilization of solid state polymerization (SSP) technology to deliver high quality restabilized PBS grades, preliminary SSP runs using severely aged prepolymers gave very promising results, in terms of molecular weight and thermal properties recovery.

FINAL REPORT: POTENTIAL IMPACT AND THE MAIN DISSEMINATION ACTIVITIES AND EXPLOITATION OF RESULTS

Dissemination activities

In order to promote the adoption of the new packaging material by the industry, the SUCCIPACK consortium implemented a strong dissemination strategy intended to a large audience including scientific community, industry, policy makers, civil society and Medias. Many web and press releases have been written and published in professional magazines and websites. Ten scientific articles were published: 2 thesis, 4 peer reviewed publications and 4 papers in proceedings of a conference. The consortium participated in 20 scientific events and organised five information relays and three technological open days. These events were a good opportunity to present the results of the project (with samples of PBS packaging) and the recommendations presented hereafter.
In addition to all these activities, a web site has been developed, www.succipack.eu, and a video highlighting SUCCIPACK outcomes, created by the consortium, is available on the home page.

Recommendations to biotechnology industry

The environmental impact of PBS production is quite important. As a comparison, the impact is greater than that of PET, despite the renewable origin of succinic acid. One reason is the scale of production; the second is the specific impact of the monomer recovery at the end of fermentation process.

- **Enlarge the uses of succinic acid** will help the development of high scale production. Despite succinic acid is a Top reference building block for chemistry, its applications apart from the plastic sector are poorly worked
- **Improve the succinic acid monomer recovery step** is an essential point both for environmental and economic considerations. Different routes were studied in the project ; one is to reconsider entirely the biotechnological route

Another aspect in the production of PBS is the route for the production of butanediol. Today, considering the higher interest in the development of succinic acid, the choice is generally to convert succinic acid into butanediol by hydrogenation; but more interesting routes should be developed considering a **direct biosynthesis of butanediol**.

Recommendations to polymer industry

Another origin of the quite high impact of PBS production is linked to the low scale of polymer synthesis.

- **Enlarge the uses of PBS** should help the development of high scale production lines. PBS should find a good development in:
    - <u>Agricultural mulch films</u> which represent a large part of plastic film market; in this application, the main default of PBS which is its fast degradability, is a great advantage.

- Commodity products. For these applications hydrolysis stabilizers can be used (long plastic shelf life is realistic) and PBS can easily substitute PP and HDPE

- **Diversify the factory productions**: today the model of polymer factories is characterized by very specialized high scale lines dedicated to the production of a specific polymer. An alternative model should be to invest in flexible lines adapted to the production of aliphatic polycondensates.
- **Consider the option of a two-step production, by melt condensation followed by SSP:** this route could support also the ability to multiply the types of grades (branching, block copolymers). This route makes consistent the idea of using large scale production and the need to develop a wide variety of grades

One of the issues for the flexible use of PBS by transformers and end users is its sensitivity to hydrolysis. As shown in the project, the degradation rate depends on the acidic index, the water content, and temperature. At the level of polymer synthesis the **good control of end chains** is essential to manage a low acidic index. Another obvious point is the residual water content in the material; generally decreased at very low concentration during the synthesis, the water content can be unfortunately increased again during post operations such as pelletizing or inappropriate storage. A dedicated **quality approach should be applied to maintain the water content under appropriate limits**, depending on material shelf life

The benchmarking of PBS revealed a limited number of references compared to other materials. More critical is the absence of some essential grades, dedicated to important applications:

- Development of **branched** and /or high IP grades, dedicated to film blowing applications.
- Development of soft copolymers with a limited decrease of Tf (**low comonomer content**)
- Development of low melting copolymers for sealing applications **(high comonomer content)**

As a last recommendation, efforts must be put on the reduction of PBS overall migration: (i) by reducing the oligomer content (thanks to synthesis conditions or thanks to post treatment after polycondensation) (ii) and as migration is also linked to the degradation state, by applying the recommendations linked to the limitation of the sensitivity to hydrolysis

Recommendations to compounding and additive industries

Different blends and compounds showed various interests for the packaging applications tested in the project and should be commercially developed:

- **Blends with PLA** at low content for good compatibility bring a modulus increase and a decrease of migration for injected packaging;
- **Blends with talc** bring a modulus increase, a better control of crystallisation, and an increase of barrier properties;
- **Blends with soft polyesters** such as PBSA improve the film blowing extrudability.

The stabilization of PBS can be better controlled by the commercialization of appropriate grades:

- Stabilization to oxidation is only necessary for transformations at high temperature (injection above 190°C)
- Stabilization to hydrolysis is a key issue which has no efficient technical response in the current commercial offer of food contact additives.
- At least as no efficient stabilization is today possible by the formulation with an appropriate additive, the compounding operation could be used to correct the material quality : (i) ensure a low water content in the final product (ii) for some degraded grades, an increase of viscosity (spontaneous repairing) was sometimes observed after simple extrusion

Recommendations to plastic converters

More than other polymers, PBS exhibit very different processing and final properties, as a function of its chemical composition (homopolymer, copolymers, branching), and its formulation with other components. A careful selection must also be done on the basis of deliverable D2.7

The second essential point to consider is the quality control of the material regarding its degradation state. In deliverable D2.7, different points are suggested:

- The use of calculation tool to calculate the M_w decrease (material lifetime prediction as a function of initial acidic index, initial M_w, water content, temperature)
- The use of quick test for the qualification of degradation state by a smart material labelling
- Recommendations of best M_w range for the main plastic transformation processes
- Recommendations for appropriate storage conditions.

Recommendations to coating industry

Coatings can bring two improvements to PBS properties:

- Better gas barrier properties
- Lower migration (functional barrier effect)

The project studied mainly the improvement of **gas barrier properties**. Organic coatings allowed barrier improvement factors up to 4, and mineral coatings allowed barrier improvement factors up to 10:

- Elaborated water based coatings were studied by Topchim and Vito. For a good adhesion of coatings, a surface pre-treatment such as oxygen plasma is necessary. Water based coatings were shown to be sensitive to the contact with water ; as a consequence (i) the coatings are preferably put on the external side of the packaging film (ii) two different coatings are difficult to apply on the same surface ; for the combination of water barrier and oxygen barrier , water barrier can be put on the internal side of the packaging, and oxygen barrier on the external side

- Mineral coatings were tested with contrasted performances (high performances of SiOx when applied on PBSA , no performances of SiOx and CxHy coatings when applied on PBS); technical R&D efforts will have to be put to be able to generalise the use of these process on all types of PBS substrates

The use of mineral layer directly in contact with the food product should provide functional barrier effects (reduction of migration); this was not tested in the project;
R & D efforts should be devoted to this.

Recommendations to end users

Fours main factors guide the selection of a PBS packaging;

Concerning **the barrier specifications**, a selection guide of PBS packaging has been built on the basis of experimental data measured during the project; deliverable D3.2 provides graphs for the selection of a type of PBS packaging on the basis of a given water vapour and oxygen barrier specifications (from thick injected systems to thin films, from uncoated to coated systems, and from unformulated systems to compounded systems)

Concerning **the migration properties**, the following aspects have to be taken in consideration:

- Overall migration is generally higher than the migration of common materials;
- Low temperature uses (4°C storage) generally not lead to unacceptable migration level whatever the packaging type;
- Room temperature and hot uses can lead to unacceptable migration levels; in these cases thin materials should be preferred.

The cost of PBS packaging is mainly linked to the price of PBS matter pellets. As a consequence, PBS thick materials have a serious disadvantage compared to other polymer references. At the contrary PBS films are less disadvantaged by the price of material.

The concept of a shelf life for a packaging is not new; a lot of elaborated material must be used within a defined period. The novel aspects with PBS are that the shelf life can be variable depending on its composition and storage conditions. All useful information should be demanded to packaging providers: Quality control ensuring constant performances, recommendations for storage conditions, predicted packaging shelf life regarding the targeted application.

Overall, considering (i) the intrinsic middle barrier of PBS films (ii) the low migration of PBS at low temperature (iii) the economical / environmental advantages of the films compared to other materials, (iv) the need to fit material shelf life and food shelf life, **the development of PBS for food packaging applications is predicted to start with <u>film</u> packaged foodstuffs, stored in <u>cold</u> conditions, with shelf life <u>less than 2 months</u>.**
Such products have been widely tested during the project, generally showing an identical performance of PBS compared to reference packaging.

Apart from these priority markets, PBS will be possibly used for other applications: breathing copolymer films for fresh fruits and vegetables, long term storage of dried products thanks to coated films… Only one basic restriction can be considered as a definitive rule, the too low melting temperature forbids sterilization and pasteurization process.

Recommendations to recycling industry

Different elements make particular the development of recycling processes for PBS:

- Very different degradation states can be obtained at the end of a PBS cycle, which can be associated to different optimal recycling routes.
- As it is already the case with PLA, the development of PBS will be associated to the development of **numerous types of formulations**, including the possible use of PBS homopolymer, copolymers, blends with other polyesters, compounds,… Only specific sources (homogeneous composition) will be possibly targeted to close loop material recycling
- PBS shows a high degree of interaction with organic compounds; it was shown to behave the same way as low density polyethylene towards aroma sorption. Consequently a post-consumer sourcing of PBS will be **possibly highly contaminated** and will be then difficultly reintroduced in the composition of a food packaging, except to consider a very effective decontamination method

As a consequence, the three following routes of PBS recycling should be chosen in specific cases:

- **1-The total depolymerisation** could be envisaged for any type of PBS material whatever the material degradation state, the contamination by undesired products during consumer uses, and the formulation complexity. The (green) enzymatic catalysed depolymerisation route studied in the project is at low TRL for this purpose; but more classical chemical routes are already possible convert soft polyesters into monomers. This route should be developed in common with the recycling of complex PLA materials. Its advantage is the possibility to purify perfectly the monomers; as a consequence it is the only realistic route for a close loop recycling in food contact, after post-consumer collection.
- 2- The **conversion into oligomers** of this complex source is technically much easier; both enzymatic and chemical routes can be chosen to convert the initial material into functional oligomers; after this step, oligomers can be flexibly re-converted to appropriate grades by SSP or classical melt condensation. As underlined by the work done in WP1, oligomers are interesting intermediate products which can be flexibly converted into specific grades. Considering the quite undefined composition of such a material, no food contact application should be recommended. At the contrary in the case of a well-defined polymer source (i.e. not post-consumer source, and constant composition), this procedure should be compatible with a close loop recycling. For a better control of material composition, a fraction of the oligomer used should be from the virgin (well defined) material.
- 3- The **direct conversion of the degraded polymer into a repaired grade** (M_w increase + restabilization) should be made in the same conditions as the previous

route ; the only difference is the less flexibility of a process starting with an heterogeneous batch (oligomers + polymers) compared to the treatment of an homogeneous population of oligomers

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The three recycling routes should be chosen as a function of the quality of the material:

- Very heterogeneous compositions (various formulations) should be oriented to route 1
- Very heterogeneously degraded sources should be oriented to route 2
- Other materials could be recycled via route 3.

Concerning the qualification of the degradation state, a smart labelling technic has been developed during the project. When marked, the material becomes yellow when its M_w is below 100 KDa. Due to the actual price of the molecular rotor used, the smart method is only envisaged as a quality control test. But cheaper molecules with the same function should be developed as systematic markers.

Recommendations to DG SANCO

The food contact properties of PBS were studied on the basis of the R 10 / 2011, looking at monomer composition, identification of NIAS, screening the additive classically used and looking for frequent substances submitted to restrictions, determining the parameters of Piringer equation for specific migration prediction, measuring overall migration properties, and measuring organoleptic potential deviations after food packaging contact. Critical uses of PBS material were then defined on the basis of contact properties measured on the **unaged** material.

The issue is that official contact tests do not reproduce the material real degradation during its shelf life. When during a food contact test (10 days 40°C) the material can be poorly degraded, it can be highly hydrolysed during the real shelf life (1 year 20°C).
Consequently, as migration strongly increases after degradation, **the official test performed on the unaged material can be too optimistic.**

An alternative route for the migration testing of materials sensible to hydrolytic degradation was proposed in deliverable D3.5. It is based on a migration test performed at half time of the material shelf life; artificial aging approaches should be proposed for quick testing.

Recommendations for future research investigations

New scientific questions were opened during the project; the following are the main subjects which should be further studied:

- The stabilization of soft polyesters to hydrolysis, by efficient/safe by design additives (physic chemical and toxicological approaches)
- Organic and mineral functional barriers to reduce the migration of highly interacting materials such as soft polyesters

- The hydrolysis properties of PBS as an opportunity for a fine controlled release for active packaging applications
- The optimization of SSP process on low melting temperature polymers
- Repairing of objects by SSP / recrystallization (cf PBS melting temperature increases of more than 10°C)
- Agricultural mulch film applications of recycled PBS and soft polyesters.