SUCCIPACK

DELIVERABLE 2.7

ACTIVE, INTELLIGENT AND SUSTAINABLE FOOD PACKAGING USING POLYBUTYLENESUCCINATE

GUIDELINES FOR PBS MATERIAL FLEXIBLE PROCESSING

MAIN AUTHOR

THE FRENCH NETWORK

OF FOOD TECHNOLOGY INSTITUTES (ACTIA)

DATE OF PUBLICATION

OCTOBER 2014

THE RESEARCH LEADING TO THIS PUBLICATION HAS RECEIVED FUNDING FROM THE EUROPEAN UNION'S SEVENTH FRAMEWORK PROGRAMME (FP7/2007-2013) UNDER GRANT AGREEMENT N°287634

Coordinator ACTIA

SEVENTH FRAMEWORK PROGRAMME

SUCCIPACK
Development of active, intelligent and sustainable food PACKaging using Polybutylenesuccinate

Project co-funded by the European Commission within the Seventh Framework Programme *(2007-2013)*

Deliverable 1.1 – Version

Nature of the deliverable		
R	Report	X
P	Prototype	
D	Demonstrator	
O	Other	

Dissemination Level		
PU	Public	X
PP	Restricted to other programme participants (including the	
RE	Restricted to a group specified by the consortium (including the	
CO	Confidential, only for members of the consortium (including the Commission Services)	

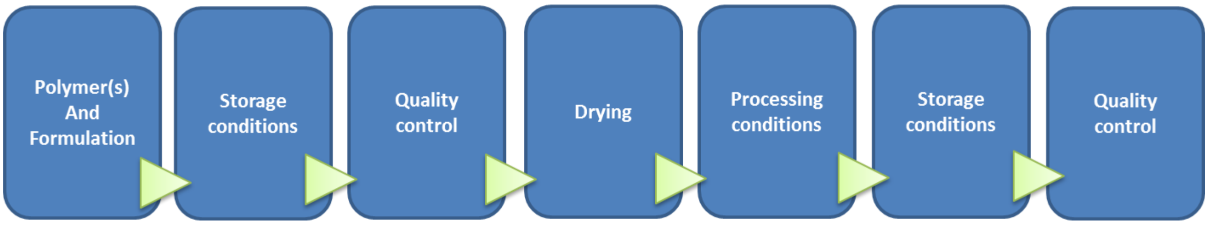
Table of content

This project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement No.289196

1. INTRODUCTION

The aim of this deliverable is to propose guidelines for a flexible transformation and provide processing conditions of PBS packaging materials.

The guideline is structured on the basis of PBS technological transformation steps from the choice of the best material for a given application to the last quality control prior to the distribution of the empty packaging.

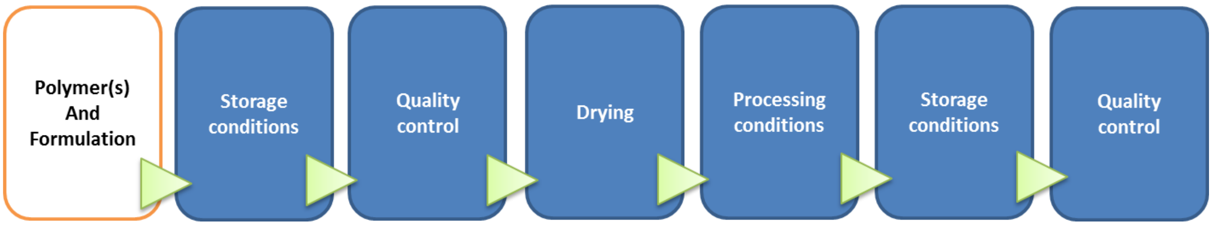


PBS is sensitive to hydrolysis, as a biodegradable polymer: a special attention must be paid to the specific steps of storage and quality control, as during storage, aging could jeopardize the processability and / or the final packaging properties.

2. RESULTS / DELIVERABLE CONTENT

As many polymer materials, but specifically for PBS, PBS based materials can show a wide range of properties through the modulation of their chemical structure and their formulation. The selection of the resin and its formulation is also a critical step to manage the material processability and the final packaging properties

2.1 PBS and PBS formulations



2.1.1 PBS grades

PBS grades adapted to various processes are available on the market, with viscosities (and subsequent Melt Flow Index) adapted to standard plastic processing methods.
As a generic rule used in the industry, the following MFI should be favoured:

This project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement No.289196

- extrusion blowing: MFI<0,5g/10 min – Branched polymer structure and / or a high polydispersity index improves also the film blowing processability ; such specific grades are not commercially available, and the improvement of PBS processability is today only possible via formulation (see next §)
- extrusion/foil extrusion: 2g/10 min<MFI<10g/10min
- injection moulding: MFI>20g/10 min

Current existing PBS grades are well adapted to the following processes:
- **extrusion**
- **foil extrusion**
- **thermoforming**
- **injection moulding**

However no specific PBS grade for extrusion blowing has been developed yet.

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

2.1.2 PBS formulations

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

Other options might be considered however the ones proposed retain two PBS advantages:
- biodegradability according to European standard EN 13432
- food contact aptitude

Blending with PLA
PLA is a glassy polymer at room temperature. As an aliphatic polyester, it shows an acceptable compatibility with PBS, especially at low contents.
Blending PBS with PLA leads to the following:
- A weak cohesion of the blend is observed for PLA contents higher than 20 wt%.

This project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement No.289196

- A particular behaviour is observed with PLA contents lower than 15%: a reduced viscosity and a non brittle behaviour are obtained.

For packaging applications, contents lower than 15 wt% should be considered, to improve PBS processability in injection moulding and thermoforming, while maintaining an acceptable level of properties.

Blending with talcum powder
Blending with talcum powder leads to:
- an increase in rigidity (needed for thermoforming)
- an increase in crystallization kinetics (needed for injection moulding)
- a decrease in material cost

However at contents higher than 20 wt%, mechanical behaviour is affected (increased brittleness). Lower contents should be advised if material flexibility is needed.

Blending with TPS
Blending with TPS leads to:
- an increase in the modulus
- an improved crystallization kinetics
- a processability behaviour intermediate between pure PBS and PBS with mineral fillers

However TPS is more sensitive to water than PBS. TPS contents should remain lower than 15 wt% to maintain barrier properties. Contents above 15 wt% also dramatically affect PBS mechanical properties and a low melt cohesion.

Blending with PBSA
PBSA is a very soft polyester easy to transform for extrusion film blowing application. Its addition to PBS leads:
- to softer materials for film applications
- to an easier film blowing processability

A monotonous improvement in processability is observed with increasing PBSA contents.
Addition of PBSA leads to a strong decrease in modulus, leading to a soft material with poor barrier properties. Contents lower than 25 wt% should be considered for film applications.

Blending with PBAT
PBAT is a very soft polyester easy to transform for extrusion film blowing application, similarly to PBSA. Its addition to PBS leads:
- to softer materials for film applications
- to an easier film blowing processability

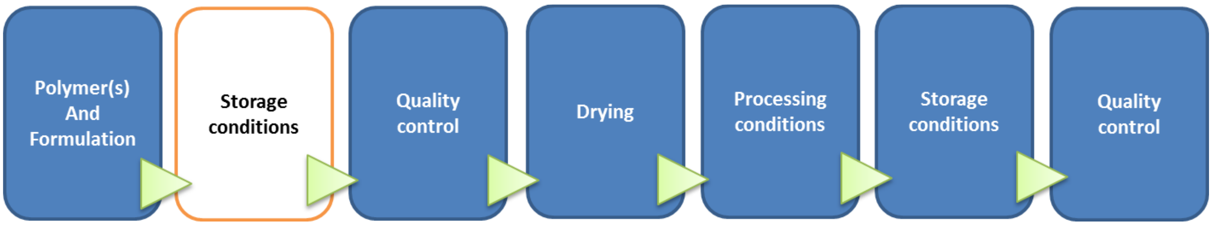
A monotonous improvement in processability is observed with increasing PBAT contents. PBAT is more flexible, compared to PBSA. Lower PBAT contents (below 15 wt%) should be favoured for film applications.

This project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement No.289196

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**

2.2 Storage conditions of polymer or compound pellets



The storage of PBS based materials is a critical step as ester bonds can be easily broken by a hydrolysis reaction, leading to a reduced molecular weight (Mw). The decrease of the molecular weight leads to an increase of the MFI, causing the transformation of:

- A film blowing grade to an extrusion grade
- An extrusion grade to an injection grade
- An injection grade to a unusable material, showing weak mechanical properties

To transform and use a material with adapted properties the best is to limit or (better) inhibit the material degradation.

The control or the inhibition of the degradation implies the knowledge of PBS degradation kinetics.

A simple kinetic model was tested in the project. The decrease of Mw is assumed to follow the equation 1:

$$\ln (Mw / Mw0) = - k\, t$$

With

- Mw0 the initial Mw
- t the degradation time
- k the degradation rate constant

k is assumed to be proportional to
- the water concentration in the material
- the initial acidic index (catalysis effect of acid end chains)
- a temperature activation factor (Arrhenius type)

By measuring the degradation kinetics in different conditions of water content, initial acidic index, and degradation temperature, a model was validated for PBS homopolymer.

Figure 1 shows the Mw decrease in different typical conditions of degradation, illustrating the importance of the 3 variables:

- The initial acidic index is managed by the first resin provider. **The selection of a low IA resin** is a very important point. The provider must be able to give the information

- The **water content** is certainly the most important variable to control and different factors can affect the level of the water content:

    - The initial process of the material, just after synthesis, leads to an initial water content which depends on the pelletization mode, a post drying step, equilibration in contact with ambient humid air before conditioning…

    - The packaging water barrier performances; **high barrier properties are required for the conditioning of <u>dried</u> PBS**. But if PBS is insufficiently dried during the previous step high barrier packaging becomes not necessary. And if the water content is higher than the water equilibrium concentration in the storage conditions, the use of a barrier packaging could have a negative impact on the material degradation, as water excess is trapped in the material

    - The environmental humidity is not an important factor if the packaging barrier is well sized. At the contrary, when the packaging barrier is undersized, a fast equilibration between external and internal water activity may occur, leading to an increase of water content

    - The material formulation (compounds) can affect drastically its water sorption properties

- **Temperature accelerates the degradation rate,** <u>at constant water content</u>. But as all polymers, at constant relative humidity, water sorption decreases as a function of temperature. This contributes to limit the temperature effect on the degradation, when a sample is heated in a non hermetic or non barrier conditions.

This project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement No.289196

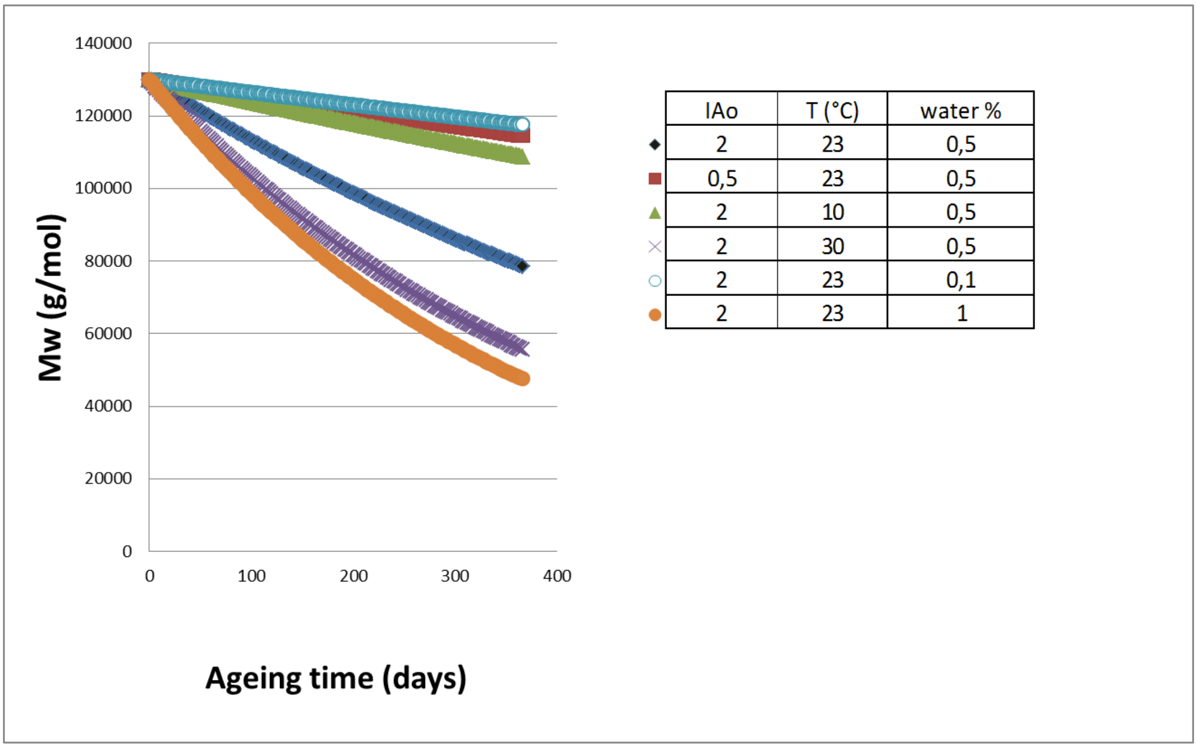
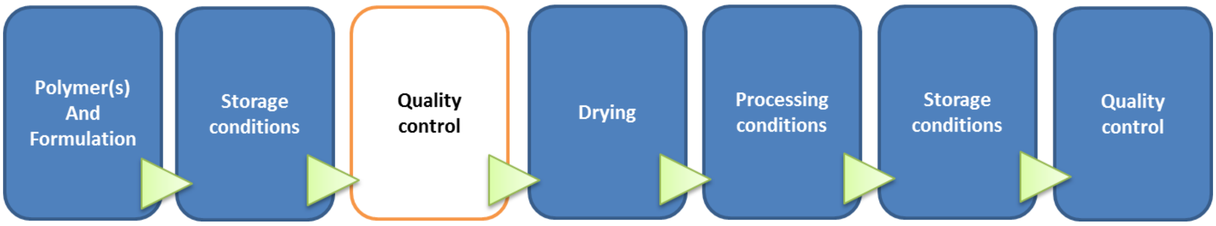


Figure 1: degradation kinetics of PBS in different cases of initial IA, water content, and temperature ;

Considering that the lowest acceptable Mw for extrusion is 120000g / mol, and 100000 g/mol for injection, maximum storage times can be deduced from the examples given is figure XX with both end life criteria

2.3 Quality control of polymer or compound pellets



The predictive tool proposed in 2.2 is difficult to use in all situations as:

- The initial Mw, IA and water content are not systematically known
- The aging conditions may be variable or not well defined
- The barrier performances of the pellet bags may be affected by packaging defaults, causing water content variability

Different parameters could also be controlled to qualify the degradation state of PBS:

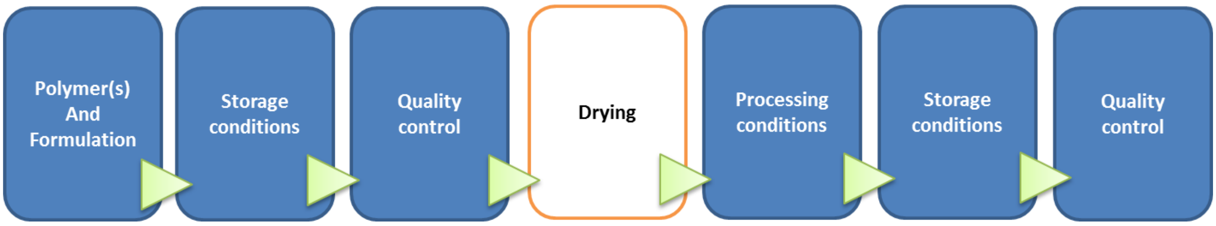
- **MFI or Mw** : Mw is a precise parameter, better than MFI for low degradation rates (when MFI is low). However MFI is more easily measured by plastic converters
- **IA and water content** are complementary criteria, not only to qualify the degradation, but also for the prediction of the next steps of material degradation

- **A smart color test** was designed during the project as a quick /inexpensive tool for quality control. It is based on the variation of the fluorescence properties of a molecular rotor dispersed in PBS, before and after aging. If the sample is yellow after the test, molecular weight is probably under 100000 g/mol ; it has to be further analysed. This test could be applied before other measurements

	New PBS	Aged PBS
Doped film with CCVJ		

Figure 2 : CCVJ smart test ; procedure: 1g polymer sample is doped with ccvj probe (72301, sigma) using a ratio probe/polymer of 100 ppm (by weight). The mixture (probe + PBS) is dissolved in dichloromethane at 40 °C over night. A polymer film was then prepared by casting (until CH_2Cl_2 remove)

2.4 Drying of polymer or compound pellets



2.4.1 PBS pellets

Polyesters such as PBS are sensitive to hydrolysis. Prior to any processing, **PBS pellets should be dried 4 hours at 80°C** in an oven or a dessicator.

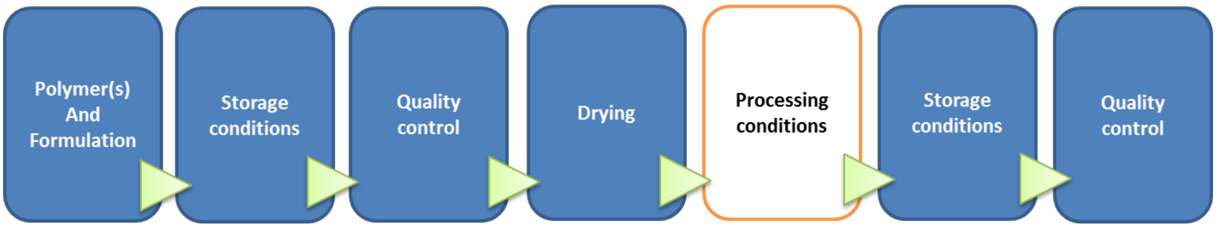
2.4.2 PBS-based compound pellets

Similarly to PBS pellets, **PBS-based compound pellets should be dried prior to processing during 4 hours at 80°C**.
Special attention should be given however in two cases:

This project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement No.289196

- **Depending upon the PBSA grade chosen for blending, drying temperature should be lowered accordingly**: some PBSA grades indeed exhibit a lower drying temperature (cf. chosen PBSA grade technical datasheet).
- **In case of blending with PLA, the drying temperature should be set up at 60°C, during 5 hours.**

2.5 Processing conditions



2.5.1 PBS grades

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

Processing method	Extrusion	Foil extrusion	Thermo forming	Injection moulding	Extrusion blowing
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	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).

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

In case of thermoforming, due to PBS softness and depending upon the depth of the thermoformed part, thicknesses above 300 µm should be preferred to obtain parts with sufficient rigidity (trays for example).

2.5.2 PBS-based compounds

The same temperature ranges are suitable for blends advised in 3.1.2.

Processing method	Extrusion	Foil extrusion	Thermo forming	Injection moulding	Extrusion blowing
Type of	All except	PBS-talcum	PBS-talcum	PBS-talcum	PBS-PBSA

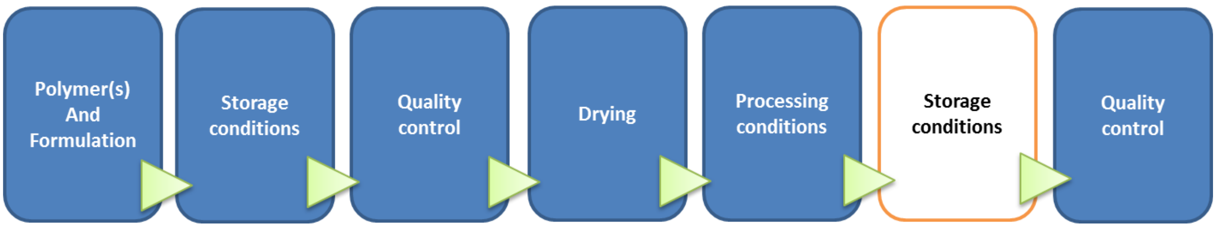
SUCCIPACK This project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement No.289196
AN FP7 PROJECT ON ACTIVE, INTELLIGENT AND SUSTAINABLE FOOD PACKAGING USING POLYBUTYLENESUCCINATE
Coordinator ACTIA

blends	with PLA			PBS-TPS	PBS-PBAT
Temperature range	110-130°C	110-130°C	105-115°C	130-150°C	110-130°C
Comments	Cooling in water Standard pelletizing			Mould at ambient temperature	

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	

2.6 Storage conditions of packaging

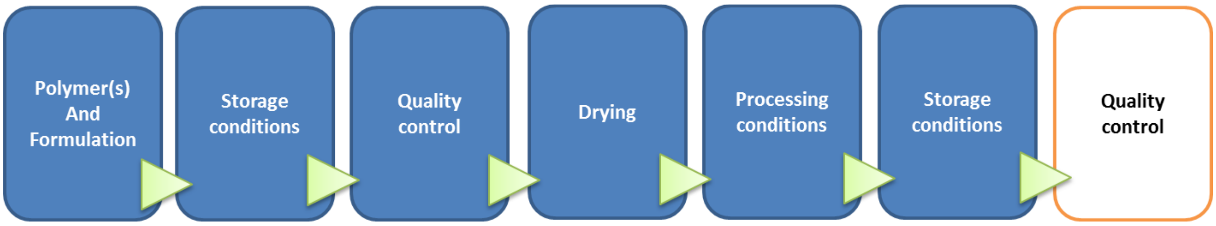


The same variables listed in 2.2 for the storage of granules have an effect on the packaging degradation, i.e. the acidic index, the water content, and temperature

- At this stage of the technological chain acidic index can be no more controlled
- Water content can be limited by a fast conditioning in water barrier bags just after processing
- Storage temperature may be also maintained below 30°C

2.7 Quality control of packaging

The same tests as proposed in 2.3 could be applied. The difference is the criteria for the rejection of the material: at this step of the technological chain, end life criteria no more depends on the material processing mode, but on the packaging properties. Degradation mainly affects migration and mechanical properties ; as a quality control, mechanical properties may be more easily measured by plastic converters or by their customers.



3. DISCUSSION AND CONCLUSIONS

This deliverable proposes guidelines for a flexible transformation of PBS. It includes:

- Recommendations for material selection
- Recommendations for conditions of transformation
- Recommendations to manage or limit the material degradation by hydrolysis during storage steps

SUCCIPACK This project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement No.289196