



DELIVERABLE 3.5

ACTIVE, INTELLIGENT AND SUSTAINABLE FOOD PACKAGING USING POLYBUTYLENESUCCINATE

**RECOMMENDATION GUIDELINES FOR THE SAFETY ASSESSMENT
OF PBS-BASED MATERIALS ACCORDING TO 1935/2004/EC**

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SUCCIPACK

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P	Prototype	
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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)	

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1. INTRODUCTION

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 /dm² 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
- Traceability requirements

The purpose of this document is to provide the data, answers, and necessary adaptations, to apply these requirements to PBS packaging materials

2. RESULTS / DELIVERABLE CONTENT

2.1 Basic components

2.1.1 Typical composition of PBS based materials

Monomers

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) No 10/2011.

Processing aids

The use of additives providing lubricant properties is often necessary to transform PBS and PBS/PBSA grades by extrusion or injection; classical additives of the positive list are efficient

Stabilization to oxidative degradation

The aliphatic structure of PBS with CH₂CH₂ and CH₂CH₂CH₂CH₂ groups confers sensitivity to oxidation. This reactivity with oxygen is only critical at high temperature (during synthesis or during injection process), because during the shelf life of the material, hydrolysis degradation kinetics are much more quicker than oxidation kinetics. Antioxidants should also be used in some specific cases; classical additives of the positive list fill the technical specifications.

Stabilization to hydrolysis and chain extenders

Obtaining and preserving long macromolecules is a key issue for the performances of PBS materials. This challenge involves special requirements:

- During PBS synthesis, the second step of “post condensation” requires the use of *chain extenders*; a particular attention to the nature of these additives (belonging to positive list) has to be paid, as a lot of non-food contact approved substances exist in this category.
- During the shelf life of the material, hydrolysis degradation must be controlled in order to limit the losses of material properties. A first approach is to control the degradation without the use of additives: decrease the acidic index (acid end chains play the role of hydrolysis catalysts), limit the residual water after processing, control the storage conditions all along the technological chain (temperature and humidity effects). The second approach is the use of specific additives (e.g. carbodiimides), which react with acid end chains; a particular attention must be paid with these formulations which are generally not developed for food contact applications, and if a specific additive is used, it must belong to the positive list.

Polymer blending

Due to the price of aliphatic polyester a lot of material developments involve the use of polymer blends. Generally the incorporation of polar polymers such as starch derivatives not confers good migration properties and should be avoided for food contact except short contact time applications. But whatever the type of the blend, if a specific dispersing or compatibilising additive is used, it must belong to the positive list.

2.1.2 Procedures for analysis

When all the information is not available about the composition (purpose of identification for positive list, requirements or purpose of determination of initial concentrations for the calculation of specific migration), it can be necessary to extract the material for further analysis of potential migrants by chromatographic and/or spectroscopic methods

Two approaches could be proposed for the total extraction of PBS based materials:

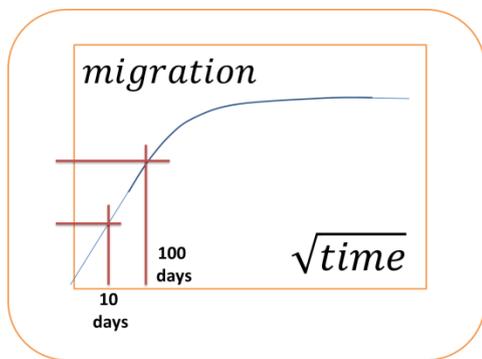
- 10 days / 60°C immersion in 95% EtOH is generally sufficient to extract to the plateau most of specific migrants, whatever the thickness of the material. To ensure that the extraction is total, a second extraction can be realized in the case of thick materials (more than 600 µm).
- Quicker procedures should be used by dissolution / precipitation methods. The issue is not the dissolution solvent (e.g. dichloromethane) as a lot of solvent candidates can be used with PBS, but the substance recovery during the steps of precipitation / substance extraction. As the procedure depend on the type of additive no recommendations will be made in these guidelines

2.2 Migration testing

2.2.1 Polymer hydrolysis issues

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 behavior:

- Classical migration kinetic decreases 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 the regulation migration tests of Regulation (EU) No 10/2011 are defined.



- 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 behavior of the unaged material.

Consequently we suggest evaluating the migration of the unaged (as suggested by the EU regulation) and of 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.

Note 1: If any demonstration is done, showing that no evolution of material property is predicted to occur during this ageing, the additional migration test has not to be realized.

Note 2: As the additional migration test is more severe than the classical one:

- It has not to be performed if the classical test is negative;
- It can be performed as a substitution test of the first one.

Note 3: The interest of a two-step evaluation is the following: if test 1 (unaged) is positive and test 2 (aged) is negative, possible restrictions of use may be considered.

2.2.2 Intended conditions of use / time-temperature conditions for migration tests

Due to a melting point at 110°C, thermal treatments of sterilization but also pasteurization should be avoided with PBS based material.

Consequently most of the uses of PBS will be covered by the contact conditions of 10 days 40°C or 10 days 20°C for the overall migration test (so called MG1 and MG2 in EU regulation 10/2011).

2.2.3 Choice of food simulants

The choice of food simulants defined by Regulation (EU) No 10/2011 is generally not a problem except in the two following cases:

- PBS and PBS based materials strongly interact with ethanol water mixtures which are defined as reference food simulants in Regulation 10/2011. In most of the cases the resulting absorption of ethanol simulates correctly the high interaction of PBS with fatty food: this absorption leads to a plasticization of the material increasing the diffusion properties in a similar manner to the effect of fatty food. But if this sorption of ethanol is too high, the test is closed to an extraction, which implies a *swelling* of the material. This effect of ethanol has been also discussed about PET. After long debates looking for criteria for the qualification of food simulant “severity”, we chose not to question the relevance of the ethanol water mixtures for PBS, because this is not a specific issue for this particular material.
- Migration in vegetal 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. 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 total, leading to result of negative calculated overall migration values. This issue was attributed both to the high level of oil sorption, and to a possible reactivity with the material. This anomalous behavior was not systematically observed. Consequently we suggest to perform two migration tests to evaluate the migration in contact with fatty foods:

Test	Issue	Advantage
In vegetal oil	High oil interaction which can lead to errors in the final calculation of overall migration (underestimation)	Realistic food simulant
In ethanol	Too aggressive food simulant	No possible analytical artefacts

In the case of a drastic difference (more than a factor 3) between the ethanol test and oil test, the oil test should not be considered as representative; consequently only the result of ethanol test should be considered.

In the case of a lower difference between the ethanol test and oil test, only the result of oil test should be considered.

Note: other solvents could be used in substitution to vegetal oil. The issue is their much higher interaction compared to ethanol. This is why particularly isooctane is not advisable as substituting solvent in the case of PBS migration testing.

2.2.4 Data for mathematical simulation 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 describe by a constant diffusion coefficient D (ii) a partition at packaging food interface described by a partition coefficient K.

Due to a volume / volume ratio between food and packaging generally more than 10, migration at equilibrium is generally considered totally in food, whenever the affinity of the migrant toward the food product is low. Consequently the prediction of migration is often considered controlled not by D and K, but only by D.

The key issue is then 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 (see Applicability of generally recognized diffusion models for the estimation of specific migration in support of EU Directive 2002/72/EC C. Simoneau, ed.).

$$D_p^* = 10^4 \exp \left[A_p^* - 0.1351M_r^{2/3} + 0.003M_r - \frac{R \cdot 10454}{R \cdot T} \right] \quad (\text{cm}^2/\text{s})$$

where: $A_p^* = A_p'^* - \frac{\tau}{T}$

- where: M_r : relative molecular mass of migrant (Dalton)
- T : temperature (K)
- $A_p'^*$: an upper bound polymer specific diffusion parameter
- τ : a polymer specific "activation energy" parameter (K)
- $R \times 10454$: $E_{A,ref}$ - reference activation energy (K)

The data measured in Succipack project allowed the evaluation of the values of the values of τ and $A_p'^*$:

τ	$A_p'^*$
-827	4.5

The variation of the diffusion coefficient with M , as predicted with these parameters and as measured in the project, is shown on figure 1. As already observed in literature, the Piringer equation proposes generally a too high overestimation for high molecular compounds. But as this ensures better the consumer safety, this is generally accepted.

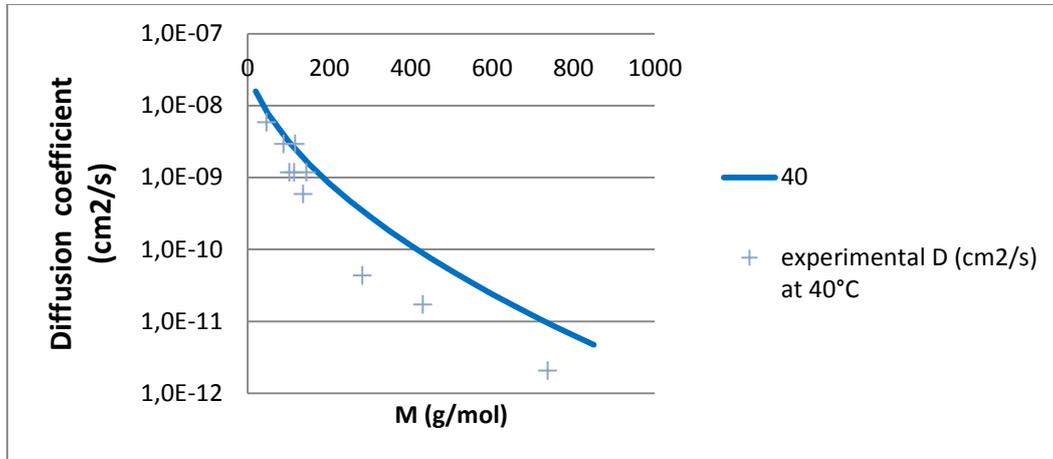


Figure 1: overestimation of diffusion coefficient in PBS at 40°C with the Piringer equation adapted to PBS with $Ap^*=4.5$ and $\tau=-827$

This equation has to be applied only for pure PBS material in low interaction with food.

In other cases such as PBSA copolymers, PBS+PBSA blends, PBS based materials highly interacting food, other Ap and τ parameters should be used. **In a first approximation, the Piringer equation parameters of polypropylene could be used in a worst case approach.**

2.3 Analysis of non-intended added substances

PBS materials show systematically a complex composition including the following components:

- Type 1 : aliphatic ester-ether derivatives resulting from simple degradation reactions and recombinations from PBS oligomers and or from its monomers;
- Type 2: Cyclic compounds generated from additional mechanisms from type 1 substances;
- Classical additives from positive list.

If a substance is identified outside of these three families, an assessment (expertise, modeling, toxicological activity test) is recommended.

3. DISCUSSION AND CONCLUSIONS

This document proposes guidelines for the safety assessment of PBS materials:

- Typical migrants to look for, to ensure all the composition information are exchanged between providers and customers;
- Choice of food simulants;
- Data for specific migration modelling;
- Typical migrate composition, to focus on anomalous substances for an efficient analysis of NIAS.

More specifically, the fast ageing of the material by hydrolysis remains a basic question: What is the representativeness of a migration test on the unaged material?

Therefore, an additional migration test coupled to an accelerated ageing test was proposed in these guidelines.