Properties of PBS

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).	

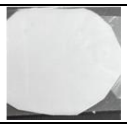
By measuring the degradation kinetics in different conditions of water content, initial acidic index, and degradation temperature, the model was validated for PBS homopolymer. To reduce the degradation rate of PBS materials, it was also necessary to minimize the initial acidic index, the water content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

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

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.

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