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**

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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.

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