

## "Reduction of the intrinsic fragility of industrial poly(lactic acid) – PLA formulations by using blending and compatibilization techniques"

In the last years, a remarkable increase in the sensitiveness about environment has been detected. As a consequence, many research works have been focused on the development on new environmentally friendly materials. This interest has been particularly remarked in the field of polymer technology, in which, the increasing use of biopolyesters is slowly invading several industrial sectors. Among these polyesters, polylactic acid (PLA), which can be obtained from renewable resources such as starch, has been gaining relevance at the same time that its price is continuously decreasing. Currently PLA is a biopolymer of great relevance in technological sectors such as automotive, construction and building, medical sector, 3D printing, and so on, among others. PLA shows excellent mechanical properties and good thermal stability. In addition, it offers a wide processing window that allows the manufacture of parts and components avoiding or minimizing its thermal degradation. However, PLA is a polymer with high crystallinity and this has a negative effect on its ductile properties. This is characterized by low elongation at break, low tenacity and, consequently, high fragility.

This doctoral thesis focuses on the improvement of the ductile properties and reduction of the intrinsic brittleness of PLA to expand, even more, its industrial applications. Although different approaches are being investigated: plasticizing, copolymerization, reactive extrusion and blending, this doctoral thesis focuses on the reduction of brittleness by obtaining ternary blends with other biopolyesters in order to obtain highly environmentally friendly formulations and a set of balanced properties. For this, the hypothesis of using a biopolyester that maintains the resistant mechanical properties in high values is proposed. In this case, we have worked with poly (3-hydroxybuturate) - (PHB), obtained by bacterial fermentation. The other working hypothesis focuses on the use of various flexible biopolyesters that could provide good impact resistance, thus increasing the tenacity of industrial formulations. To this end, various flexible bio-polyesters such as poly (ε-caprolactone) - (PCL), poly (butylene succinate) - (PBSA) are used.

Considering the relevance of miscibility phenomena on final properties of polymer blends, the use of a series of compatibilizing agents derived from renewable natural resources is considered. In particular, this research reports the use of modified vegetable oils (epoxidized and maleinized). Thus, considering the reactivity between the epoxy, maleic anhydride and acrylic acid groups with the terminal hydroxyl groups present in the polymer chains of the different biopolyesters, it is possible to hypothesize the improvement of the miscibility/interaction between the different polymers in ternary blends by using epoxidized, maleinized and acrylated soybean oil (ESO, MSO and AESO respectively).

Overall, the results obtained in this doctoral thesis, allow to expand the potential use of the PLA through ternary blends with PHB and PCL or with PHB and PBS or PBSA. The formulations developed in this research work significantly improve the tenacity of the PLA, which allows to significantly reduce its intrinsic brittleness.