

SUMMARY

“Development of polylactic acid (PLA)-derived formulations by plasticization and additives from renewable resources”

The main objective of this doctoral thesis is the study, development and characterization of biodegradable or biocompatible materials from poly(lactic acid) (PLA) with improved properties for uses in several sectors such as food packaging, medical sector, etc. In order to modify the ductility and the stiffness of PLA, with the subsequent effects on its potential uses in different sectors, different fillers and/or additives were incorporated to PLA formulations by extrusion. Several plasticizers derived from vegetable oils and fatty acids were used; particularly, an epoxidized plasticizer derived from stearic acid (octyl epoxy stearate – OES) and a maleinized linseed oil – MLO were used. Another strategy that has been used in this research has focused on the development of binary blends with other polymers with increased ductility such as polycaprolactone (PCL) and thermoplastic starch (TPS). Finally, incorporation of several biocompatible/resorbable fillers derived from calcium orthophosphate ($\text{Ca}_3(\text{PO}_4)_2$) such as β -tricalcium phosphate (β -TCP) and hydroxyapatite (HA), was carried out to widen the potential of these PLA-based materials in medical applications.

Initially, physical blends of PLA with flexible biodegradable polymers (PCL and TPS) with a maximum content of 30 wt% of them, were obtained by extrusion/compounding and subsequent processed by injection moulding. The obtained results suggest slight differences in ductility as both binary systems seem to show restricted miscibility. The elongation at break is higher for the system PLA/PCL. Nevertheless, PLA's crystallinity increases with small TPS loads. It is worthy to note that the energy absorption is better for the PLA/TPS system compared to the counterpart compositions of the PLA/PCL system. This phenomenon is directly related to the low miscibility of PLA and PCL. Although pure starch is also immiscible with PLA, its commercial thermoplastic form includes some plasticizers and an aliphatic/aromatic biodegradable polyester that contribute to improve PLA/TPS interactions. As a consequence of this relatively low miscibility between binary PLA/PCL and PLA/TPS blends, the main thermal transitions do not change in a great extent.

Regarding the use of plasticizers from vegetable oils and fatty acids, the obtained results show interesting potential for industrial PLA formulations with improved ductility. By using octyl epoxy stearate (OES), a noticeable decrease in the glass transition temperature (T_g) and in the cold crystallization temperature (T_{cc}) occurs together with a remarkable increase in the elongation at break ($\epsilon\%$) and the energy absorption in a Charpy's test. In addition, the overall crystallinity increases due to the higher chain mobility. These materials have been also processed in a film form and show lower oxygen permeability and a higher hydrophobicity. No important changes in thermal stability were observed. On the other hand, slow amounts of maleinized derivative from linseed oil (MLO) allowed reaching higher elongation at break values than those obtained with OES, as well as a remarkable improvement on impact behavior without compromising the overall stiffness properties. The increase in chain mobility that MLO provides allows reducing the T_g and the cold crystallization peak temperature (T_{cc}) and this has a positive effect on crystallinity thus leading to materials with both improved ductility and stiffness. In addition to the excellent plasticization properties that MLO provides, this research assesses its potential as compatibilizer agent in the binary PLA/TPS blend with relatively low MLO amounts in the 2-8 phr. These compatibilized blends offer a homogeneous morphology and show a direct relationship between the overall impact-absorbed energy and MLO content. With regard to resistant properties, they keep almost constant with similar values to those of the uncompatibilized PLA/TPS blend. All these PLA-based materials with plasticizers and blends with other polymers offer interesting flexible properties, which widens its potential in the packaging industry.

Finally, the effect of different biocompatible/resorbable fillers from orthophosphates (β -TCP and HA) on mechanical, thermal and thermomechanical properties was evaluated with the aim of increasing the potential of these PLA-based formulations in the medical sector. Both particles show a nucleant effect on the cold crystallization process thus leading to increased stiffness on composites. Although both reinforcing fillers offer similar performance, some differences can be seen regarding other properties. So, in terms of thermal stabilization, HA has a positive effect on PLA while β -TCP leads to lower thermal stability due to its high hygroscopic behavior. From a mechanical performance standpoint, good-balanced mechanical resistant properties are obtained with PLA formulations with 30 wt% β -TCP and HA.

With this doctoral thesis, the technologic potential of PLA formulations for industrial applications in the packaging industry is increased by using natural-derived plasticizers from vegetable oils and binary blends with flexible, biodegradable polymers such as PCL and TPS. On the other hand, addition of orthophosphate fillers into PLA matrix increases the potential of this polymer in the field of medical devices due to their biocompatibility and resorbability.