
Miscibility, rheological and thermo-mechanical properties of compatible biopolymer blends: influence of process parameters and natural surfactants

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Abstract

In the recent years, a growing interest in biodegradable plastics as an alternative to the conventional fossil fuel-based polymeric materials was developed. Particularly, PLA is broadly applicable for use as an alternative to petrochemical- derived products. In fact, this polymer is biodegradable and biocompatible and its properties are very similar to those of some synthetic fossil fuel-based polymers. Nevertheless, the range of application of PLA is limited due to its fragility, poor barrier properties and the limited temperature range at which it can be used. Various strategies were proposed to overcome these limitations, such as modifying the chemical structure of the polymer with plasticizers or blending with other polymers. In this work a polylactic acid PLA (70 wt%) and poly- hydroxy butyrate PHB (30 wt%) blend was prepared to obtain a bioplastic with mechanical properties intermediate between those of the two polymers. Specifically, the aims of the work were improve the miscibility of the blend and increase the thermo-mechanical properties. Two different approaches were used to achieve these goals: the study of the influence of process parameters and the introduction of natural compatibilizers in the blend. For the first, a co-rotating twin screw extruder LEISTRITZ ZSE 18/40D ($\Phi = 18$ mm, $L/D = 40$) was used with three different screw profiles. The investigated formulations were: unfilled PLA/PHB blend and containing 5 wt% of an organo-modified clay (Cloisite 5). In the second part two types of natural surfactants with different chemical structure were used: an ethylene oxide/propylene oxide block copolymer (Synperonic) in the form of flakes and a mixture of two liquid surfactants with a variable lipophilic–hydrophilic index (HLB 12). In this case, PLA/PHB blends were prepared using a DSM Explore twin screw mini-extruder ($T=180^{\circ}\text{C}$ and screw speed=100 RPM). The investigated formulations were: PLA/PHB with HLB12 ranging from 0.1 wt% to 5 wt% and PLA/PHB with Synperonic in the same range of content. Morphological, thermo-mechanical and rheological analyses were performed on each formulation in both case studies. Firstly, a correlation between the observed morphology and the screw profile was found; in particular, the milder screw profile was the best solution. This result is supported by rheological analyses: an increase of the storage modulus (G') was obtained after the adding of Cloisite, while the unfilled PLA/PHB blend exhibits a shoulder in the G' curve caused by the relaxation of the dispersed phase which is in form of droplets, showing the typical rheological response of an immiscible blend. In the second part of the study, the

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morphological and the rheological analyses showed that HLB 12 was more effective than Synperonic. In fact, the trend of G' in this last formulation was similar to that of the uncompatibilized blend. Conversely, samples containing HLB 12 showed a different trend of G' curve and a decrease of the curve slope in the terminal region can be observed, as well. This behaviour can be attributed to the obtainment of a complex morphology, significantly different from that of the neat blend PLA/PHB. Nevertheless, while for HLB 12 system, it was necessary the use of a solvent for their introduction into the extruder, the Synperonic presents the advantage of introducing a solid additive during the process. As far as the thermo-mechanical analyses are concerned, both types of compatibilizers induced excellent mechanical properties at high temperatures, resulting in an increased HDT value that allows to widen the application range of the obtained materials.

Keywords: PLA, PHB, polymer blends, rheology, small amplitude oscillatory shear