Characterisation of poly(lactic acid) self-reinforcement and its influence on material morphology, crystallinity and properties

I. Trofin[1*], M. Borůvka[2], D. Kaineder[1,3], S. Hild[1]

[1] *Institute of Polymer Science, Johannes Kepler University, Linz, Austria*
[2] *Faculty of Mechanical Engineering, Technical University of Liberec, Liberec, Czech Republic*
[3] *Competence Center CHASE GmbH, Linz, Austria*
[*] *ingrid.trofin@jku.at*

Poly(lactic acid) (PLA) is a bio-based, biodegradable material that has shown great potential as an alternative to fossil-based polymers. PLA is biocompatible and has favourable physico-chemical properties (e.g., optical, mechanical, barrier) that are comparable to those of synthetic, commercially-available polymers, with PLA already being used in biomedical, industrial and commercial applications. However, its low thermal stability and low impact strength are disadvantageous for further technical applications [1].
The current study proposed a solvent-free methodology, using the PLA stereocomplex (PLA-SC) between enantiomeric poly(D-lactic acid) (PDLA) and poly(L-lactic acid) (PLLA) to achieve material self-reinforcement. The stereocomplexation is driven by the intermolecular hydrogen-bonding established between the $-CH_3$ and O=C groups of the single components. Due to the resulting compact domains, the stereocomplex has a greater thermal stability than the PLA homopolymers [2]. The PLA-SC was produced in a 1:1 D/L ratio, post-annealed, then incorporated in low amounts (1, 3, 5 wt.%) into PLA matrices of different optical purities, i.e., D-isomer content. This compounding was done at three PLA-SC threshold melting temperatures, in order to alter the strength of the internal hydrogen-bonding within the stereocomplex crystallites by partially melting them.
The influence of PLA-SC on crystallinity and morphology was investigated, in relation to mechanical and rheological properties. An increase in crystallinity with the addition of PLA-SC was indicated by differential scanning calorimetry (DSC) and confirmed by Raman spectroscopy for both matrices (PLLA and poly(D,L-lactic acid) (PDLLA)). The self-nucleation effect of the stereocomplex was remarked under the thermo-optical microscope (POM), where the pellets were isothermally crystallised at 120 °C. An increase in the percentage of PLA-SC resulted in a notable rise in the number of nuclei and an initial formation of bigger semi-crystalline structures. Atomic force microscopy (AFM) measurements, further performed on the thin-films so-obtained via POM, revealed two distinct morphologies correlated to the crystallinity trends recorded, namely spherulites and shish-kebabs, the latter being known as flow-induced, oriented semi-crystalline conformations. Rheology measurements showcased the effect of the stereocomplex stability on the PLA behaviour under deformation, while mechanical tests showcased its effect on the PLA behaviour under stress. The heat deflection temperatures (HDT) also registered an increase for both PDLLA and PLLA, proving that the HDT values of the PLA materials were governed by their crystallinities and that the low dimensional thermal stability of PLA could be overcome.
The incorporation of low amounts of PLA stereocomplex into PLA matrices of different optical purities under industrial processing conditions led to the self-reinforcement of PLA and the concomitant improvement of material properties, without compromising its positive life cycle assessment.

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