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PLA-PHA BLENDS: MORPHOLOGY, THERMAL AND MECHANICAL PROPERTIES

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Introduction

Biotechnological polymers such as polylactides (PLA) and polyhydroxyalkanoates (PHA) are alternatives to petroleum-based polymers and represent an attractive growing market. These sustainable polymers are becoming more competitive due to the increase of the price of the oil barrel and overall concern about the limits of petrol feedstock. However, the polymers from renewable resources have often serious disadvantages as compared with conventional synthetic polymers. One is poor mechanical properties which limit their practical applications. Blending of polymers is a useful way of obtaining new materials with improved properties, which can overcome the drawbacks of the pure components. The physical and mechanical properties of blends can be tuned by choosing the proper polymers, varying the composition of the blend and preparation conditions.

Most of the studies on PLA and PHA blends that have been reported in the literature concern the blends prepared by solvent casting. Only few studies have been conducted on the preparation and characterization of PLA/PHA blends by melt mixing [1] despite the fact that both polymers are thermoplastics and their processing is similar to the classical oil-based polymers. In the present research work, blends of a polylactide and a poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) prepared by melt-mixing have been studied.

Experimental

The PLA/PHBV blends were prepared by melt mixing in an internal batch mixer (Haake Rheomix 600). The PLA/PHBV compositions tested were 0/100, 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, 90/10 and 100/0 (w/w).

Results and Discussion

Differential scanning calorimetry was used to study the miscibility and thermal properties of the PLA/PHBV blends. The glass transition and melting temperature of PLA and PHBV were almost constant for all the range of compositions tested and coincided with transition temperatures of the pure components. It was concluded that the PLA/PHBV binary blends are immiscible in the melt.

The blend morphologies were investigated using a scanning electron microscope (SEM). Blends with a minor phase below 30 wt% showed a nodular structure. For example, Figure 1a presents a SEM micrograph of a fractured surface for a 70/30 PLA/PHBV blend. We clearly distinguished spherical droplets of PHBV in the PLA matrix.

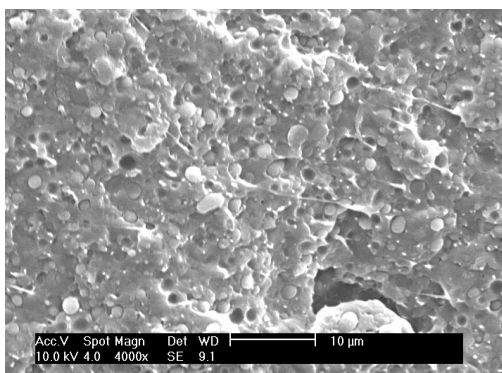


Figure 1a – SEM micrograph of a PLA/PHBV fractured sample with weight ratio 70/30

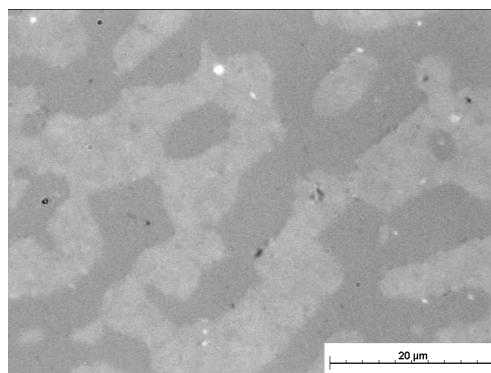


Figure 1b – Optical micrograph made in reflection mode of a PLA/PHBV polished sample with weight ratio 50/50

On the contrary, 60/40, 50/50 and 40/60 blends seemed to exhibit a co-continuous structure, which was confirmed by microscopy in reflection on polished samples as shows Figure 1b.

The rheology of the pure polymers and of the blends was investigated in the dynamic mode. It was demonstrated that thermal stability of PHBV is extremely low: complex viscosity dropped by more than one decade in one hour. Dynamic frequency sweep tests were carried out to characterize the viscoelastic properties of the PLA/PHBV blends at 175°C. A “shoulder” for G’ was observed for PLA/PHBV blends and correlated to a significant role of polymer-polymer interphase.

Tensile tests were performed for all the blend compositions. The samples (ISO 527 - Type 1BA) were injected with a mini injection moulder (Haake Mini-Jet II). Pure PLA and pure PHBV had similar mechanical characteristics: small elongation at break (about 4%) and similar Young’s modulus. Figure 2 shows the evolution of the elongation at break as a function of PLA weight fraction in the blends. For the majority of the blends, the mechanical behaviour was similar to the one of the pure components. However, we observed a significant necking for compositions containing PHBV as dispersed phase (10 and 20 wt%). The PLA/PHBV 90/10 blend exhibited substantial ductile plastic deformation: elongation at break reached more than 200%. The same phenomena has been observed with blends of PLA and poly(hydroxybutyrate-co-hydroxyhexanoate) (PHBHx) [2]. The difference is that PHBHx is much more ductile than PHBV used in this study. Possible mechanisms of this interesting effect will be discussed.

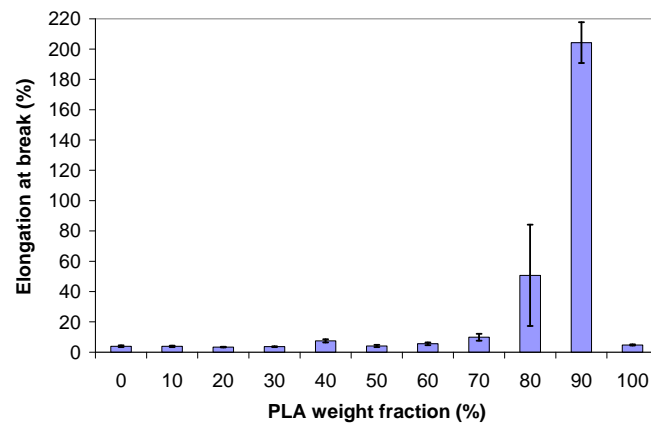


Figure 2 – Elongation at break as a function of PLA weight fraction in the PLA/PHBV blends

Conclusion

Blends of PHBV and PLA have been prepared by melt mixing. Blends morphology, thermal and mechanical properties were investigated by electron scanning and optical microscopy, DSC, oscillatory rheometry and tensile experiments. The DSC showed the immiscibility of the two polymers for all compositions. Two different morphologies have been observed: nodular and co-continuous structure depending on blend composition. Rheology showed that thermal stability of PHBV was extremely low and that interfaces played a significant role in PLA/PHBV blends. Although PLA and PHBV are both brittle polymers, blends containing a small amount of PHBV in a PLA matrix showed a significant ductile plastic deformation.

Acknowledgments

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