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Preparation and characterization of Polyhydroxyalkanoates (PHA) and Polylactide (PLA) blends

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Abstract. Polylactide (PLA) and poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) blends were prepared in different compositions by melt mixing. The miscibility of the two components was first characterized by differential scanning calorimetry (DSC) experiments, which showed the immiscibility of the components for all blend compositions. The morphology was studied using scanning electron microscope (SEM) and optical microscopy in reflection. Nodular and co-continuous morphologies were observed depending on the composition. The rheology of the pure polymers and of the PLA/PHBV blends was investigated in the dynamic mode. The results showed a significant role of the interfaces with an increase of the complex viscosity at small frequencies.

Introduction

Nowadays, petrochemical based polymers are associated with a lot of environmental concerns and sustainability issues. An important part of those polymers are used for short-lived applications by the packaging industry. When these materials are incinerated, they participate to the release of CO₂ in the atmosphere, which increase the greenhouse effect and the global warming. Moreover, a non negligible part of the plastics accumulate in the oceans and impact the ecosystems. Biotechnological polymers such as polylactides (PLA) or 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. The capacity for the production of biobased plastics, which was estimated at 300 000 tones in 2008, is expected to reach more than 3 million tones in 2020 [1]. Polyhydroxyalkanoates are polyesters directly produced by numerous microorganisms by bacterial fermentation of sugars or lipids. These microorganisms accumulate PHA as water insoluble inclusions in their body as a carbon and energy storage material [2]. Polylactide is synthesized from lactic acid, which is obtained from renewable resources such as corn, starch or maize. Polylactide is now produced on a large scale and used for various applications in different domains: packaging, medicine, agriculture, textiles…

The blending of polymers is a useful way of obtaining new materials with improved properties, less costly than chemical modifications or synthesis of tailor-made copolymers. The physical and mechanical properties of blends can be easily modified by choosing the polymers and varying the composition of the blend. 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 [3] 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 poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) and a polylactide have been studied. These blends have been prepared by melt-mixing of the initial polymers in various proportions. The aim of this study is to understand the thermal, morphological and rheological properties of PLA/PHBV blends.
EXPERIMENTAL

Materials

PHBV was purchased from Tianan Biological Materials Co. Polylactide (3051D, injection molding grade) used in the study was supplied by NatureWorks Co. Ltd., USA.

Blend preparation

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).

Methods

Thermal analysis was performed on a Perkin Elmer DSC 8500 differential scanning calorimeter in order to assess the thermal properties of the blends ($T_g, T_f$) and to study the miscibility of the two components system. The samples were first heated from -40°C up to 200°C at a heating rate of 10°C/min under nitrogen atmosphere and maintained at this temperature for 2 min to eliminate thermal history. The samples were then cooled to -40°C at a cooling rate of 10°C/min and heated again to 200°C at 10°C/min.

RESULTS AND DISCUSSION

Miscibility of PLA/PHBV blends

Differential scanning calorimetry was used to study the miscibility of the PLA/PHBV blends. The melting temperature ($T_m$) of the two blending partners remained constant and independent of the blend composition. Two main melting endotherms were found at around 150 and 170°C, corresponding to the melting temperatures of PLA and PHBV.

The glass transition temperature ($T_g$) of PLA was around 60°C and did not show any variation with the blend composition. The determination of the glass transition temperature of the PHBV was difficult with the chosen heating rate; however, $T_g$ of PHBV could be evaluated to 4°C.

The glass transition and melting temperature of PLA and PHBV were almost constant for all the range of compositions tested, showing that the PLA/PHBV binary blends are immiscible in the melt.

Thermal degradation of PHBV

It is known that polyhydroxyalkanoates have a very narrow processing window because of their thermal degradation, which limits their commercial use. Thermal degradation occurs rapidly at a given processing temperature, which is very close to the melting temperature. For instance, the acceptable residence time for poly(3-hydroxybutyrate) in the processing equipment is only a few minutes [4].

The rheological data obtained in our study showed clearly that thermal stability of PHBV is extremely low. Fig. 1 displays the evolution of the complex viscosity of PLA and PHBV as a function of oscillatory shear time at 175°C. The decrease of the viscosity of PHBV is dramatic: $\eta^*$ dropped by more than one decade in one hour.

The thermal degradation was confirmed by the assessment of the molecular weights of PHBV samples using a gel permeation chromatography (GPC) kindly performed by Arkema. The PHBV samples were collected after dynamic tests lasting different times. $M_m$ was divided by two after a 10 min test and by four after one hour of rheological experiment. This decrease of molecular weight with test time can be attributed to the decrease of the polymer length via chain scission.
Morphology observation

The blend morphologies were first investigated using a scanning electron microscope (SEM). Fig. 2 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. Besides, the adhesion between the two phases was bad. Blends with minor phase below 30 wt% showed a nodular structure. On the contrary, 60/40, 50/50 and 40/60 blends seemed to exhibit a co-continuous structure.

Due to the similar structure of the two polyesters, the contrast between the two phases was limited. Moreover, selective dissolution did not work. To observe the morphology of the PLA/PHBV blends more clearly, samples were finely polished and observed with a microscope in reflection. Fig. 3 shows an image of a 50/50 blend sample. This blend showed a co-continuous structure, with two interpenetrated phases. The same morphology was observed for the 40/60 and 60/40 compositions.

Rheological behavior of the blends

Dynamic frequency sweep tests were carried out to characterize the viscoelastic properties of the PLA/PHBV blends at 175°C. Fig. 4 displays the elastic modulus ($G'$) and the complex viscosity ($\eta^*$) curves for the pure polymers and their blends in different compositions (20/80, 50/50 and 80/20).

Firstly, both $G'$ and $\eta^*$ were the highest for pure PLA and increased with the PLA content in the PLA/PHBV blend. The elastic modulus of the pure PLA (100/0) and the pure PHBV (0/100) showed a typical terminal behavior with a slope of around 2 at low frequencies (Fig. 4a). For the blends containing a small quantity of PLA or PHBV, we clearly observed a shoulder for $G'$. It should correspond to the relaxation of droplets of the dispersed phase in the matrix. We noticed the formation of a $G'$ plateau at low frequencies for the blends containing nearly as much PLA as PHBV. Interfaces between PLA and PHBV play thus a very significant role in the rheological behavior of the blend. This is supported by the significant increase of the complex viscosity at low frequencies for the 50/50 blend (Fig. 4b).
Fig. 4. (a) Dynamic storage modulus (G’) and (b) complex viscosity (η*) of PLA/PHBV blends as a function of oscillatory shear frequency (T=175°C)

Conclusion
In this study, blends of PHBV and PLA have been prepared by melt mixing. Miscibility, phase morphology and rheological behavior were investigated by DSC, SEM and oscillatory rheometry. The DSC experiments showed the immiscibility of the two polymers for all compositions. Two different morphologies have been observed: nodular structure and co-continuous structure. Rheological testing has showed that thermal stability of PHBV was extremely low and that interfaces played a significant role in PLA/PHBV blends. Work on the effect of adding a commercial compatibilizer on the rheological and morphological properties of PLA/PHBV blends is in progress.

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