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Miscibility and Transport Properties of Poly(lactide)/Phenoxy System

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Summary: The addition of Phenoxy to Polylactide causes a decrease of the permeability coefficients proportional to the amount of Phenoxy, even in spite of the lack of miscibility between both polymers. The effect of a Poly(caprolactone-b-lactide) multiblock copolymer as a compatibilizer of a Poly(lactide)/Phenoxy blend was analyzed,[1] achieving miscibility and providing an improvement in the barrier properties of the blend.

Keywords: blends; block copolymer; compatibilization; poly(lactide)

Introduction

Poly(lactide) (PLA) has attracted increasing attention as a biodegradable thermoplastic for general usage in degradable disposables. In packaging industrial applications it is necessary to improve the barrier character of this material. The poor mechanical and barrier properties are its main drawbacks for packaging applications. However, these properties are necessary in order to preserve organoleptic food quality during its shelf life because they prevent the alteration of food due to excessive oxygen or water vapor transference or the loss of aromatic compounds.[2,3] Much work has been undertaken to improve PLA transport and mechanical properties.

Blending PLA with Phenoxy [4] could be an appropriate alternative to improve oxygen and carbon dioxide barrier character in PLA. The two polymers are immiscible, but the lack of miscibility can be overcome with the presence of a multiblock (L-lactide-co-ε-caprolactone) copolymer (PLCL) that could act as a compatibilizer in the blends[5] due to the known miscibility between PCL and PH.

The aim of this work is to study the transport properties of the PLA/PH inmiscible blend and also to analyze the effect of the addition of a multiblock copolymer in those properties when the miscibility is achieved.

Experimental Part

Poly(lactic acid) was supplied by Natureworks and Poly(hydroxy ether of bisphenol A) by Union Carbide with a molecular weight of approximately 162500 and 50700 g/mol, respectively. Copolymer was synthesized in bulk polymerization with stannous octoate as initiator. Block character (η) of copolymer is approximately 0.5, which corresponds to a multiblock structure with a 54% (mole) of ε-caprolactone and a molecular weight of approx. 142600 g/mol.

All the blends were prepared using the following procedure. First, the two polymers were premixed in a molten state in the desired compositions 0, 25, 50, 75 and 100% by weight. After that, all compositions in molten state were mixed in a Model CS -183 MMX mixer operating at 40 rpm at 190 °C during 4 min. Scanning electronic microscopy (SEM) samples were obtained from these extrudates after gold coating on cryogenically fractured surfaces.

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Furthermore, membranes for sorption measurements were prepared by compression molding using a Graseby Specac hot-pressing device at 190 °C under 90 bar pressure. Thicknesses between 50–80 μm were obtained and measured by a Duo-Check ST-10 apparatus. Membranes were kept in vacuum for at least 7 days before carrying out the corresponding measurement.

Glass transition and melting temperatures were measured by a differential scanning calorimeter using a TA Instrument DSC Q2000 V24 calibrated with an indium reference standard and purged with dry nitrogen gas. This device operates at sub-ambient temperatures with a RCS (Refrigerated Cooling System), the RCS 90 can be used for experiments requiring cooling within an operating range of −90 °C to 550 °C.

The DSC thermograms were obtained for a heating rate of 10 °C/min, the glass transition temperature was analyzed on the second scan after melting the sample at 200 °C to destroy any previous thermal history.

Hitachi S-2700 SEM equipment was used at an accelerating voltage of 15 kV.

A single gas permeation test for direct measurement of the carbon dioxide permeation properties in polymeric membranes was built in our laboratory, similar to other devices described in bibliography.[6] Before starting the measurement, the whole system was vacuumed for at least 12 h to remove any residual gas to obtain accurate measurements.

Penetrant gas was then introduced in the upstream side at a constant pressure of 760 Torr in the feed chamber, whereas the downstream pressure in the permeate chamber was directly measured with a MKS Baratron Type 627B Absolute Pressure Transducer, which can provide pressure measurements in the range of 10 Torr to as low as 0.02 Torr.

From the curve slope of the pressure at the permeate side versus time, *dp/dt* (Torr/s), when steady state was achieved, the gas permeability coefficient was calculated by the following equation:

$$P = \frac{(dp/dt)\,LV\,T_{STP}}{p_A p_{STP} T A}$$

Where P is the permeability coefficient of a membrane to carbon dioxide in barrer, V is the volume of the downstream chamber (cm^3), A is the effective area of the film (cm^2), L is the thickness of the membrane (cm), T_{STP} and p_{STP} are the standard temperature and pressure (273 K and 76 cm Hg), p_A is the pressure of the penetrant gas in the upstream chamber (Torr) and T is the temperature of the measurement (298 K).

The oxygen permeability coefficient was obtained using a Mocon OX-TRAM 2/21 MH model at a pressure of 1 atm, 23 °C and 0% of relative humidity. The Mocon equipment directly gives the oxygen transmission rate (OTR) that is related to the permeability coefficient by the following expression:

$$OTR\left(\mathrm{cc\ mil/m^2 day}\right) \times (0.294/p(\mathrm{mm\ Hg})) = P(\mathrm{Barrer})$$

Results and Discussion

The miscibility of the blend was studied by a differential scanning calorimeter (DSC) and scanning electron microscopy (SEM). The glass transition temperatures and the compositions used in the blends are summarized in Table 1. The compositions without compatibilizer show two glass transition temperatures corresponding to pure polymer values, so the PLA/PH

Table 1.
Thermal properties of PLA/PH blends and PLA/PH with PLCL as compatibilizer.

SAMPLE	Tg (°C)
PLA	54
PLA/PH 75:25	54/92
PLA/PH 50:50	54/91
PLA/PH 25:75	54/91
PLA/PH/PLCL 40:40:20	45 broad single Tg
PH	90

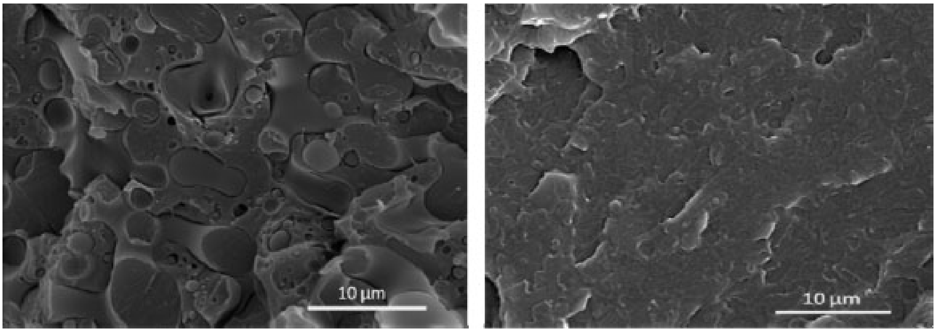

Figure 1.
SEM micrographs of PLA/PH 50:50 and PLA/PH/PLCL 40:40:20.

system seems to be completely separated in two phases as confirmed by the SEM micrograph of PLA/PH 50:50 (Figure 1a).

The efficiency of a multiblock PLCL copolymer as a compatibilizer in PLA/PH blends was investigated by the following PLA/PH/PLCL 40:40:20 composition. When the multiblock copolymer was added, the glass transition temperatures converged into a single broad Tg, which is related to the decrease of the size of the dispersed phase. The SEM micrograph also shows a homogeneous appearance, so it can be concluded that the miscibility of the blend is achieved.

Apart from the glass transition temperature, the first scan of DSC in both, binary and ternary systems showed that samples remained practically amorphous, thus the effect of crystallinity was not taken into account in this study.

Transport properties are directly related to the free volume of the material. Immiscibility can promote the generation of additional free volume, specially located in the interface, so it is a suitable property to show if there is good adhesion between the two bonding interfaces on the blend.

In Figure 2, permeability coefficients to carbon dioxide and oxygen are shown. Although the molecular size of oxygen is smaller than that of carbon dioxide, the capacity of condensation of CO_2 is larger leading to a higher permeability.[7]

Permeability coefficients not only show a decrease proportional to the amount of Phenoxy, but also a slight negative deviation from the additive rule. Consequently, the lack of miscibility is not relevant in this system.

However, the addition of a 20 wt % of the multiblock copolymer to the blend is able to reduce the permeability coefficient of the immiscible blend by the same percentage, even taking into account that both components (PLA and PCL) have a worse barrier character (PCL has a P_{O2} value of 0.9 Barrer and P_{CO2} of approx. 9.2 Barrer) than the PLA/PH blend, a good result considering that the ternary blend has 60% biodegradable polymer.

A similar result can be observed in the case of water vapor with a quantity of the copolymer in the blend, but in this case an upward curvature of the slope could suggest that a slight phenomenon of clustering[8] or plastification could be happening. These two phenomena can be distinguished from the behaviour of the diffusion coefficient and it will be corroborated by sorption measurements in further studies.[9]

Conclusion

Poly(lactide) and Phenoxy are immiscible polymers, as DSC and SEM micrographs have shown. The SEM displays a homogeneous appearance for PLA/PH/PLCL 40:40:20 blend in contrast with PLA/PH, which is consistent with the DSC result. Despite the immiscibility, the permeability

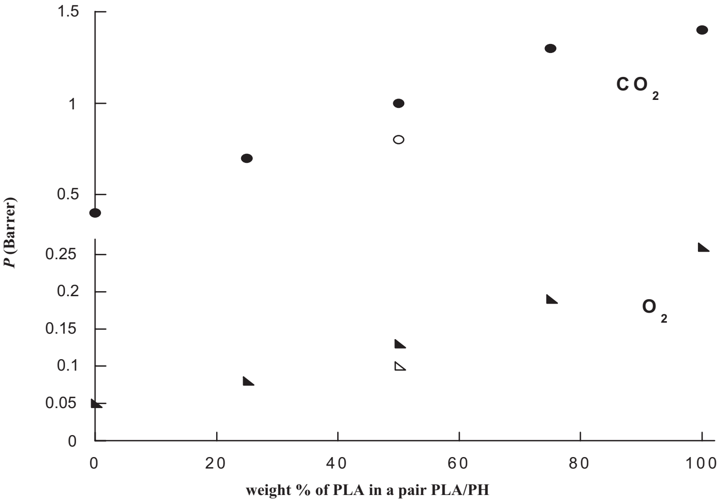

Figure 2.
Permeability coefficients to carbon dioxide and oxygen in all range of compositions of PLA/PH blends (filled markers) and PLA/PH/PLCL 40:40:20 (open markers) composition, with PLCL as compatibilizer.

coefficient in the PLA/PH fulfills the additive rule, a slight negative deviation can also be observed for oxygen and water vapor.

Transport properties confirm that in the presence of a compatibilizer agent the blends show better behaviour as barrier materials. This is due to the decrease of approx. 20% in the permeability towards carbon dioxide, oxygen and water vapour obtained using 60% of a biodegradable polymer.

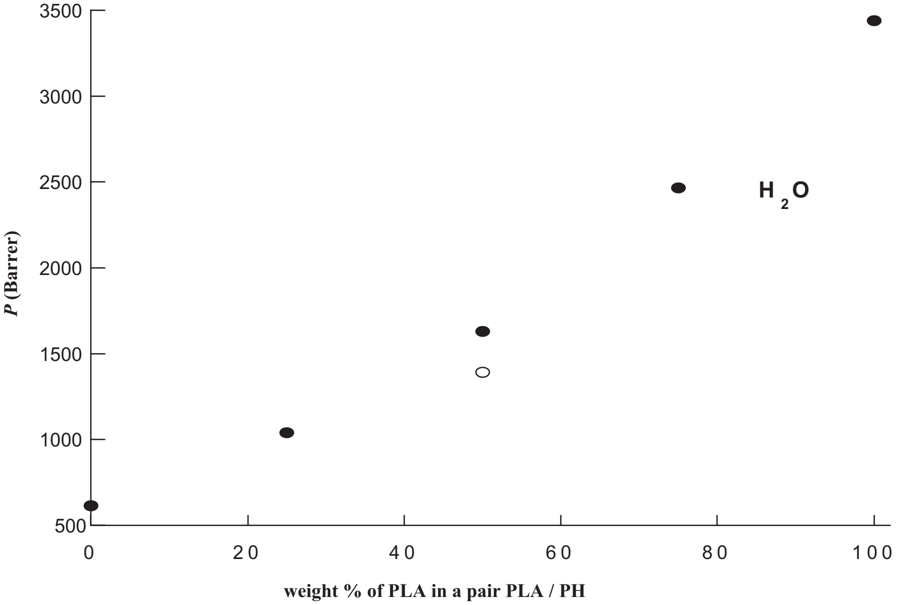

Figure 3.
Permeability to water in all range of compositions of PLA/PH blends (filled markers) and PLA/PH/PLCL 40:40:20 composition, with PLCL as compatibilizer (open markers), at 25 °C of temperature.

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