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Blends of biodegradable poly(butylene adipate-co-terephthalate) with poly (hydroxi amino ether) for packaging applications: Miscibility, rheology and transport properties

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ABSTRACT

The improvement of the properties of biodegradable poly(butylene adipate-co-terephthalate) (PBAT) through the addition of poly(hydroxi amino ether) (PHAE) is investigated. Analysis by means of DSC, DMTA, FTIR and TEM reveals that blends are partially miscible, with finely dispersed droplet/matrix morphology. Besides of morphology, hydrogen bonds between both, hydroxyl groups and tertiary amines in neat poly(hydroxi amino ether), and with carbonyl groups of poly(butylene adipate-co-terephthalate) in the blends, work out the linear viscoelastic properties and the time relaxation spectrum. Blends rich in poly(hydroxi amino ether) show the highest relaxation times and consequent strain hardening behaviour, which facilitates film elaboration for packaging.

Permeability to water vapour, limonene and carbon dioxide is measured obtaining a great reduction on PBAT permeability with the addition of poly(hydroxi amino ether), specially for carbon dioxide. The mechanical properties of the blends are similar to the polymer that forms the matrix. Overall, this work aims to shed light on the effect of a second component on the properties of a biodegradable polymer in order to design suitable materials for packaging applications.

1. Introduction

Biodegradable polymers have attracted a great attention over the last years, due to the growing awareness of the environmental problems associated to the huge volume of polymer waste. Nowadays, the employed polymers for packaging applications have a short service life and they are not degradable. Biodegradable polymers offer a potential solution, notwithstanding they have, in general, low barrier character to gases and vapours and poor mechanical properties. Therefore, polymer blending is a widely employed method in order to improve their properties [1–3].

Poly(butylene-adipate-co-terephthalate) (PBAT), generally known under the tradename of Ecoflex^R, is an aliphatic aromatic copolyester that can be fully degraded in few weeks [4]. It has good mechanical properties, such as adequate toughness and tear resistance, but it has a low barrier character to water vapour, oxygen and carbon dioxide [2]. In order to improve the properties of PBAT different approaches have been carried out being one of them blending with another polymer, for example poly(hydroxy ether of bisphenol A), which presents an outstanding barrier character, and that leads to miscible blends [5].

Poly(hydroxi amino ether) (Blox^R, PHAE), which has a similar characteristic to phenoxy, is a good candidate to improve the limitations of PBAT, since it presents an outstanding barrier quality to oxygen and carbon dioxide. It combines the great adhesion and durability of epoxy thermoset resins, with the processability of thermoplastics. It contains hydroxyl groups that can form strong specific interaction via hydrogen bonds, which leads to compatible blends [6–8]. Poly(hydroxi amino ether) polymer have been found to be partially miscible with polyamide-6 [9,10], poly(butylene terephthalate) [11], poly(ethylene terephthalate) [12] and poly(caprolactone) [13].

Since PBAT/PHAE blends are potential candidates for packaging industry, and films are obtained usually by blow extrusion, the rheological properties under shear and extensional flow must be investigated. The rheological features of immiscible blends depend on the concentration of each polymer phase, type of flow field, interaction between phases, morphology and interfacial tension between phases

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[14,15]. In the literature the relationship between rheology and morphology has been widely investigated [14,16,17]. It has been proved that the measurements performed in the linear viscoelastic regime are able to detect small differences in the morphology due to the coalescence of the droplets [18]. Some authors have tried to relate the morphology of immiscible blends with different rheological plots, like relaxation spectrum and others, with only a relative success [19,20]. Regarding the rheological properties under extensional flow, most of the works focus on the study of polyolefins, although there are a few studies on biodegradable polymers. For instance, the extensional flow of PLA has been studied [21–23].

In the packaging sector the characterization of the transport properties is a necessary task. Depending on the characteristic of the packed product different permeability to penetrants is required. For example, fruits and vegetables need oxygen for respiration whereas in other products oxygen can provoke the growth of microorganism and the oxidation of fats. In literature the transport properties of biodegradable polymers, such as polylactide, poly(caprolactone) and poly(hydroxybutyrate), have been widely studied [24–26]. Taking into account that in general biodegradable polymer present poor barrier character different methods have been used to improve this property: blending with another polymer or adding different fillers [27,28]. In the case of immiscible polymer blends the morphology also affects the transport properties [29,30].

In this work PBAT/PHAE blends are studied. Miscibility is analysed by means of Differential Scanning Calorimetry (DSC), Infrared Spectroscopy (FTIR), Dynamic Mechanical Thermal Analysis (DMTA) and Transmission Electron Microscopy (TEM). Rheological properties under shear flow, in the linear viscoelastic regime, and under extensional flow are studied and linked to the morphology of the blends and the presence of hydrogen bonds. Finally the mechanical performance and the permeability to water vapour, limonene and carbon dioxide is measured to assess the suitability of these blends for packaging applications.

2. Experimental part

2.1. Materials

Poly(butylene adipate-co-terephthalate) (PBAT) of a molecular weight Mw = 75000 g/mole, known as Ecoflex^{R}, was purchased from Basf (Ecoflex F Blend C1200). PBAT is a random copolymer with adipate/terephthalate ratio of 47/53 in mole. The poly(hydroxi amino ether) resin (PHAE) of MFI = 8.5 g/10 min at 200 °C and 2.16 kg load ASTM D-1238 was supplied by Dow Chemical, under the trade name Blox^{R}. The respective Newtonian viscosities of PBAT and PHAE, obtained as explained below in the corresponding sections, are 800 and 40000 Pa s.

2.2. Blend preparation

PBAT/PHAE blends were prepared in the molten state employing a Model CS-183 MMX mixer at 190 °C and 40 rpm. Films for permeability measurements with thickness of 60 µm and 200 µm were obtained by hot pressing using a Graseby Specac device at 190 °C. Sheets of 1 mm thickness for rheological measurements were obtained also at 190 °C by compression moulding. The membranes and sheets were dried in vacuum 2 days at 70 °C and at least 5 days at room temperature.

2.3. Differential scanning Calorimetry (DSC)

Thermal properties were measured in a differential scanning calorimeter model Q2000 V24 TA Instruments. Samples of approximately 5 mg were encapsulated in aluminium pans and two scans were performed from −80 °C to 200 °C at 10 °C/min heating and cooling rate.

2.4. Thermo-mechanical properties

Dynamic mechanical thermal analysis was performed using a Triton 2000 DMA (Triton Technology, Ltd.) in bending mode from −55 to 120 °C. The measurements were performed with a heating rate of 4 °C/min and a frequency of 1 Hz, which are commonly used to evaluate the glass transition temperature T_g.

2.5. Infrared spectroscopy

The infrared spectra were recorded in a FTIR spectrometer Nicolet Magna 560 using an ATR unit Golden Gate. The spectra were recorded with 2 cm^{-1} resolution.

2.6. Thermogravimetric analysis (TGA)

Thermal gravimetric analysis was performed using a TGA Q500 (TA Instruments) equipment. Samples of 3–5 mg were prepared and heated from room temperature to 800 °C at 10 °C/min heating rate under nitrogen flux of 100 mL/min.

2.7. Morphological characterization (TEM)

Morphological characterization was carried out employing a TECNAI G2 20 TWIN (FEI) transmission electron microscopy (TEM) with an acceleration voltage of 200 keV. The samples were cut at −50 °C using a LEICA EMFC6.

2.8. Rheological measurements

Rheological measurements were carried out using an ARG-2 rheometer (TA Instruments). Small amplitude oscillatory shear measurements were conducted under nitrogen atmosphere at 150 °C using a parallel plates geometry (diameter 25 mm). Frequency sweeps were carried out in the linear viscoelastic regime from 628 to 0.05 rad/s.

The rheological properties under uniaxial extensional flow were measured using the Extensional Viscosity Fixture (EVF) of an ARES rheometer (TA Instruments) at 150 °C.

2.9. Mechanical measurements

The mechanical properties were measured employing an Instron 5565 testing machine at a crosshead displacement rate of 5 mm/min and 22 °C. The films have a thickness between 100 and 150 µm and the specimens were cut according to ASTM D638 type V. At least 5 specimens were tested for each reported value.

2.10. Permeability measurements

Water vapour and limonene transmission rate were measured in a permeation cell at 25 °C according to ASTM E96–95 method. The cell is a small container made of polytetrafluoroethylene, which is partially filled with water or limonene and a polymeric membrane in the top. The measurements were carried out in a Sartorius BP 210 D balance with 10^{-5} g readability and the mass loss was recorded in a computer [31]. The values shown are the average of at least 5 measurements.

Carbon dioxide permeability was measured in a permeation cell built in our laboratory, which is similar to other equipments described in literature [32–34]. The measurements were carried out at 1 atm and 25 °C and the values shown are the average of at least 5 measurements.

3. Results and discussion

3.1. Analysis of miscibility

From a practical point of view, miscibility of the polymer blends is