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Material Properties

Effect of plasticizers on thermal and physical properties of compression-moulded poly[(3-hydroxybutyrate)-co-(3-hydroxyvalerate)] films

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ABSTRACT

Poly[(3-hydroxybutyrate)-co-(3-hydroxyvalerate)] (PHBV) is a promising bio-based, biodegradable polymer for replacing synthetic polymers, but its brittleness limits its application range. With the aim of improving the mechanical properties of PHBV films, different plasticizers (polyethylene glycol (PEG 200, 1000 and 4000), lauric acid (LA) and stearic acid (SA)) were incorporated into the film formulation at 10 wt%. All plasticized films showed lower melting temperature and crystallization degree than pure PHBV films. All plasticizers, except SA, reduced film stiffness and resistance to break, and increased the films' water sorption capacity and solubility as well as their water vapour permeability, but only PEG1000 yielded more extensible films. PEG1000 and PEG4000 gave rise to the most heat-resistant plasticized films, while LA and SA highly promoted the heat-sensitivity of PHBV. PEG1000 was the most effective at plasticizing PHBV films, and it was the only plasticizer that partially mitigated the ageing effects. However, a greater ratio of plasticizer would be required to adapt PHBV mechanical properties to some packaging requirements.

1. Introduction

In recent years, numerous research works have focused on the valorisation of biodegradable polymers obtained from organic waste. Materials derived from renewable sources containing polysaccharides, lipids and proteins can be consumed by microorganisms, especially by bacteria, in order to obtain monomers such as hydroxyalkanoic acids (with many structural variations) and D- and L-lactic acid [1]. These monomers have been used to produce polyhydroxyalkanoates (PHAs) and polylactic acid (PLA), respectively, two of the most important biodegradable polymers derived from renewable sources [2,3].

PHAs are a family of linear polyesters of 3, 4, 5 and 6-hydroxyacids synthesised by a wide variety of bacteria, including strains of *Pseudomonas*, *Bacillus*, *Ralstonia*, *Aeromonas* or *Rhodobacter* [4]. These polymers are present in the cells as cytoplasmic inclusions, which are used as energy reserves [5,6]. Depending on polymer composition, a wide range of PHAs with desirable properties can be obtained, from polymers which are stiff and crystalline to others that are flexible and rubbery [7].

Poly-hydroxybutyrate (PHB) is one the most widely studied PHAs [8,9]. The physical properties of PHB are often compared to those of isotactic polypropylene because they have similar melting points, degrees of crystallinity and glass transition temperatures [10,11]. PHB presents good processability, and it yields materials with a high degree of transparency and stiffness. Even if PHB has many interesting properties, its inherent brittleness, relatively low thermal stability, ageing behaviour and high cost of production restrict its range of applications [12], and thus it is often combined with other polymers such as PLA to obtain films with improved properties [13–16].

PHB's great fragility is described as a result of different factors, which also contribute to its ageing behaviour: (1) secondary crystallization of the amorphous phase since its glass transition is close to room temperature; (2) low nucleation density, which leads to "large" spherulites or the appearance of cracks in the inter-spherulitic confinements that worsen the film's mechanical properties [17,18]. In order to reduce the brittleness and thermal instability of PHB, copolymers like hydroxyvalerate (known as PHBV) have been obtained. As reported by Savenkova, Gercberga [19], these copolymers give rise to much less brittle materials, with

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higher extensibility, than the homopolymers; the higher the hydroxyvalerate content, the more flexible is the material.

Additionally, in order to reduce PHBV brittleness, different plasticizers have been used. These reduce the intermolecular forces along polymer chains, which improve the flexibility and chain mobility, at the same time that they provoke a decrease in glass transition temperature and changes in the crystallization behaviour. The effect of different kinds of plasticizers on the mechanical and thermal properties of PHBV matrices has been studied. Some of these are polyols, such as propylene glycol (PG) or glycerol (G), [20]; citrates, such as triethyl citrate (TEC) [21] and acetyl butyl citrate (ATBC) [12]; polyolefins, such as polyisobutylene [19]; dibutilphtalate (DBP) [21]; dibutyl sebacate [19]; oils and triglycerides, such as castor oil, soybean oil and epoxidised soybean oil (ESO) [20]; surfactants like sophorolipid [22] or poly-ethylene-glycol with medium molecular weight (PEG1000) [20]. In general, medium molecular weight substances with oxygen atoms (e.g. ethers or ketones), which are accessible for interactions with the polymer matrix, such as PEG1000, TEC or DBP, have effectively improved the films' stretchability [20]. The addition of some plasticizers hindered the PHB and PHBV crystallization in line with the interruption of interactions among the polymer chains [12,17,22]. However, some plasticizers, such as PG, PEG1000 or ESO, promoted molecular mobility, thus favouring the crystallization process [20].

PEGs of different molecular weight have already been used as effective plasticizers in different polymers [23–25], and could be a good alternative for PHBV matrices. No previous studies into the effect of the molecular weight of this compound on its plasticizing effectiveness in PHBV films have been found. Likewise, although surfactants, such as fatty acids, have been used as plasticizers in different matrices [26–28] their potential for PHBV plasticization has not been analysed either.

In this study, the effect of the addition of PEG with different molecular weight and two fatty acids (lauric acid or stearic acid) on crystallization behaviour and thermal stability, tensile properties and water affinity of PHBV films was characterized. In addition, the films were analysed in terms of their microstructural and optical properties, and the impact of storage under controlled conditions (ageing process) on film properties was also evaluated.

2. Materials and methods

2.1. Materials

Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) 8% (PHBV) was provided in pellet form by NaturePlast (Caen, France). Polyethylenglycol 200 (PEG200), polyethylenglycol 950–1050 (PEG1000), polyethylenglycol 4000 (PEG4000) and lauric acid (LA) were supplied by Sigma-Aldrich (Sigma–Aldrich Chemie, Steinheim, Germany). Stearic acid (SA) was obtained from Panreac Química, S.A. (Castellar del Vallès, Barcelona, Spain).

2.2. Preparation of films

PHBV films were prepared by melt blending and compression-moulding. PHBV was mixed with a constant amount of PEG200, PEG1000, PEG4000, LA or SA (10 wt % w/w with respect the total solids) on a two-roll mill (Model LRM-M-100, Labtech Engineering, Thailand) at 180 °C and 15 rpm for 10 min. Pure PHBV without plasticizer, used as control film, was processed under the same conditions. Films were obtained by pressing 3.5 g of each blend by using a hydraulic press (Model LP20, Labtech Engineering, Thailand). Steel sheets were pre-heated for 5 min and then compression was performed at 180 °C for 4 min at 100 bar, followed by a cooling cycle to 60 °C for 3 min. The films obtained were conditioned at 25 °C and 53% RH for 1 or 5 weeks (initial and final times respectively) prior to testing. In this way, six types of sample were obtained: without plasticizer (PHBV) and with the different plasticizers (PHBV-PEG200, PHBV-PEG1000, PHBV-PEG4000; PHBV-LA and PHBV-SA).

2.3. Film characterization

2.3.1. Film thickness

Film thickness was measured to the nearest 0.0025 mm with a Palmer digital micrometer at six random positions.

2.3.2. Scanning electron microscopy

The cross-section of the samples was observed using a Scanning Electron Microscope (JEOL JSM-5410, Japan). Conditioned film samples were immersed in liquid N_2, cryofractured, fixed on copper stubs, gold coated and observed using an accelerating voltage of 10 kV.

2.3.3. Differential scanning calorimetry (DSC)

DSC analyses were carried out by using a differential scanning calorimeter (Star^e System, Mettler-Toledo, Inc., Switzerland). Film samples (~7 mg) were weighed in aluminium pans and sealed. Samples were analysed using a double scan: a first heating step from -60 °C to 200 °C at 10 °C/min, then cooling to -60 °C at 50 C/min and a second heating step at 10 °C/min to 200 °C. An empty aluminium pan was used as reference. Measurements were taken in duplicate for each sample under a nitrogen stream of 20 mL/min. The crystallinity degree of the polymer in the films was estimated by using Eq. (11) from the melting enthalpy values (ΔH) of the samples (J/g PHBV) and the melting enthalpy of 100% crystalline PHB ($\Delta H^0_{PHB} = 132$ J/g polymer) [29], by assuming that only PHB crystals are formed in PHBV.

$$Xc(\%) = \frac{\Delta H}{\Delta H^0_{PHB}} \cdot 100 \tag{11}$$

Pure plasticizers were also analysed in terms of their melting properties. Thus, a cooling scan at 10 °C/min, followed by 10 min at isothermal conditions (10 °C below the melting temperature) and a subsequent heating scan at the same heating rate was applied.

2.3.4. Thermogravimetric analysis (TGA)

A thermogravimetric analyser (Star^e System, Mettler-Toledo, Inc., Switzerland) was used to measure the thermal weight loss of each type of film in duplicate in a temperature range between 25 °C and 600 °C at a heating speed of 10 °C/min under a nitrogen stream of 20 mL/min.

2.3.5. Tensile properties

Mechanical performance of the films was studied according to ASTM standard method D882 [30]. A Universal Testing Machine (TA.XTplus model, Stable Micro Systems, Haslemere, England) was used to obtain the stress–strain curves of the samples. From these curves, tensile strength (TS), elastic modulus (EM) and elongation (*E*) at break of the films were obtained. Film samples (2.5 × 10 cm) were placed in film-extension grips and stretched until breaking at 50 mm min^{-1}. Measurements (eight replicates per formulation) were considered after film conditioning.

2.3.6. Moisture content

Conditioned films (for 1 or 5 weeks) were dried for 24 h at 60 °C in a convection oven (J.P. Selecta, S.A. Barcelona, Spain) and finally placed in a vacuum oven to complete film drying. Measurements were taken in triplicate.