



Polybutylene succinate adipate/starch blends: A morphological study for the design of controlled release films



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ABSTRACT

Films made of plasticized starch (PLS)/poly(butylene succinate co-butylene adipate) (PBSA) blends were prepared by thermomechanical processing varying the PBSA proportions in blends to obtain biphasic materials with distinct morphologies. These morphologies were characterized by selective extraction of each phase, microscopic observations, and selective water/oxygen permeation properties. These experiments allowed identifying the blend compositions corresponding to the beginning of partial continuity (cluster partial percolation) until total continuity of each phases. This property was related to the controlled release of model molecule (fluorescein) previously dispersed in the PLS and revealed that its release depended on the tortuosity of the PLS phase tailored by the polymer blends composition and by the limited swelling of the PLS when entrapped in the PBSA phase. Future applications will focus on food preservatives dispersed in PBSA-PLS blends to obtain active antimicrobial packaging put in direct contact with intermediate to high moisture foods.

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1. Introduction

To overcome the limitations of passive barrier prepared with conventional formulations, the development of controlled release materials presents a growing interest achieved by the incorporation of active compounds in polymer matrices. In food, cosmetic or pharmaceutical packaging, embedded molecules play an active role to preserve the properties of the packaged products. Meanwhile, in Europe, regulation on such active packaging limited the applications and research effort for a long time (Regulation EC no. 1935/2004, EC no. 450/2009) while in modern drug delivery, strategies to optimize the release profile of the active compounds were designed (Siepmann, Siepmann, Walther, MacRae, & Bodmeier, 2008).

Amongst the studied systems, immiscible polymers blends are promising ones when used as materials or coatings. As they are immiscible (or partially miscible), polymer blends usually lead to biphasic structures with evolving morphologies playing with their composition: matrix-dispersed particle structures, matrix-fiber structures, lamellar structures or co-continuous structures. Selective solvent extraction, microscopic observations and

viscoelastic properties are usually used to investigate these blends (Castro, Carrot, & Prochazka, 2004, Schwach & Avérous, 2004). According to Pötschke and Paul (2003), the polymer blend morphology is based on the percolation concept. When the percolation occurs, one part or the totality of one of the two phases forms a continuous structure that permeates the whole sample and eventually dominates the properties of the blend. A distinction between partial continuous structures and full continuity can be made. When one phase is totally continuous, it can be traversed from side to side without crossing any interface. When the polymer phase is partially continuous, some sample areas are inaccessible (without crossing any interface).

Transport properties of such polymer blends are sensitive to changes in material morphology especially because of the percolation phenomenon which makes diffusion paths more or less tortuous (Leuenerger, Bonny, & Kolb, 1995; Romm, 2002). In fact, the blend morphology can be well investigated by permeation properties (Espuche, Escoubes, Pascault, & Taha, 1999). For example, Soney, Ninan, and Sabu (2001) studied the variation of gas permeability of membrane made of SBR (styrene butadiene rubber and natural rubber- i.e. NR-) with different volume fractions of natural rubber. They concluded that matrix-dispersed morphology makes tortuous path for the gaseous molecules until the dispersed phase (NR) becomes a continuous one and thereby enhances a sharp permeability increase. From theoretical and experimental

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approaches, Park, Cohen, and Langer (1992) concluded on a drastic permeability increase at the percolation threshold where the minor component starts to make a continuous channel across the membrane. Other authors used partially miscible blends to successfully adjust drug diffusivity, or delivery of proteins (Lyu, Sparer, Hobot, & Dan, 2005) playing with the hydration properties to activate the diffusion.

Over the last decades, literature has focused on biodegradable or biosourced polymer blends (Auras, Harte, & Selke, 2004; Woodruff & Huttmacher, 2010; Yu, Dean, & Li, 2006) involving a renewable polymer and aliphatic polyesters (PCL, PLA, PHA, PBS, PBSA, etc.), studied to achieve better physical properties (mainly mechanical properties, water sensitivity, etc.). Amongst natural polymers, starch has been widely studied because it is suitable for plastic processing (extrusion or injection) when plasticized with both water and polyols (generally glycerol) (Averous & Boquillon, 2004; Rodriguez-Gonzalez, Ramsay, & Favis, 2006) to be called Plasticized Starch or PLS. Amongst the polyesters, polybutylene succinate (PBS) and copolymers (PBSA – i.e. poly(butylene succinate-co-butylene adipate) are noteworthy because of their intrinsic thermal properties located in between polypropylene and polyethylene ones, which are the synthetic polymers frequently used as packaging materials. Moreover, PBS and copolymers are nowadays synthesized from fossil resources but are expected to be “all green” in the future as monomers can be obtained by bacterial fermentation (Song & Lee, 2006).

In this work, several blends made from polar PLS and semi-polar PBSA have been investigated to study the possible relationships between blends morphology and the controlled release of migrants/probes used as model molecules. The applications, once morphology explained, will focus on dispersion of food preservatives in blends to design antimicrobial packaging materials.

The blends morphology was thus investigated by combining information resulting from:

- (1) selective extraction of each phase enriched by microscopic observations
- (2) selective transport properties of oxygen and water vapor through gas permeation experiments
- (3) water sorption experiments (since transport can be modified/activated by water sorption of PLS)
- (4) fluorescein desorption studies.

2. Materials and methods

A series of biphasic blends made of plasticized corn starch (30wt. glycerol, on a dry matter basis) (PLS) manufactured by Clextral S.A. (Firminy, France) and PBSA, purchased from NaturePlast (Caen, France) were prepared as described below. For fluorescein desorption studies and confocal scanning laser microscopy observations, PLS was formulated with fluorescein sodium salt (Sigma–Aldrich, Saint Quentin Fallavier, France).

2.1. Blends preparation

Various PBSA/PLS blends (from 0 to 100 wt.% PBSA content, Table 1) were prepared from granules of each component. PLS granules were previously equilibrated at 50% RH and 23 °C until constant weight (i.e. for one week). The blends are denoted as follows: PBSA10 means that the blend contains 10% of PBSA and 90% of PLS. Two methods of blend preparation were used.

2.1.1. Melt blending

The melt blending was carried out in a Haake internal batch mixer Rheomix 600® (Thermo Scientific, Villebon sur Yvette, France). The mixing temperature was set to 120 °C. The roller speed

was 50 rpm. The average shear rate was estimated to be 25 s⁻¹. After 10 min mixing, the torque was found to be constant.

2.1.2. Extrusion process

2.1.2.1. PLS/PBSA blends. Extrusion was performed by two runs in a three-zone single-screw extruder (Scamex, Crosne, France) (heated at 120, 120, and 110 °C, respectively). A fourth zone at 110 °C of a vertical downright annular die was added to prepare tubular extruded films. The rotation speed of the extruder screw was set at 50 rpm which gave an approximate residence time of ~55–60 s. The sample stands issued from the first run were pelletized (Scamex pelletizer, Scamex) and, as previously described, re-extruded to get a better homogeneity.

2.1.2.2. Labeled PLS/PBSA blends. PLS phase was labeled with fluorescein sodium salt at two concentrations: 50 and 500 ppm before blending with PBSA for two purposes. Fluorescein sodium salt was added to PLS for confocal scanning laser microscopy observations of the blends (fluorescein being a fluorescent probe for PLS phase visualization) and for the release study in water, respectively. The extrusion process was the same as described in the former paragraph but starch pellets were previously sprayed by an adequate amount of aqueous solution of fluorescein sodium salt. This amount was calculated to reach the global water uptake of starch corresponding to a storage at 50% RH (i.e. 9 wt.%) (Godbillot, Dole, Joly, Roge, & Mathlouthi, 2006) and needed for starch extrusion. Moreover, pellets were conditioned at 50% RH and 23 °C for one week before extrusion.

2.1.3. Samples conditioning

All the samples prepared either by melt blending or by extrusion were conditioned (50% RH and 23 °C for one week) before being characterized.

2.1.4. Films preparation

Samples from blends were pressed molded into films by using a constant thickness film maker mold placed in a hydraulic press equipped with platens heated at 120 °C (Specac, Eurolabo, Saint Chamond, France), a 4 ton pressure was applied for 20 s. The duration of fluorescein desorption kinetics, water sorption as well as oxygen and water vapor permeability measurement experiments depended on membrane thicknesses. Therefore films with different controlled thicknesses were prepared in order to get a suitable duration for these experiments and to limit the immobilization of corresponding instruments. Typical thicknesses were around 60 ± 10 μm for measurements of fluorescein desorption kinetics with a spectrofluorimeter, 230 ± 10 μm for water sorption in a climatic chamber and 330 ± 10 μm for gas permeation (O₂ and water vapor).

2.2. Blend morphology characterization

Selective solvent extraction and microscopic observations were combined for the evaluation of the blends morphology. Before and after extraction, as previously mentioned, sample pieces (1–2 g) have been conditioned for one week at 50% RH and 23 °C before weighing (especially after PBSA removal).

2.2.1. Solvent extraction

Extraction of each polymer phase by a selective solvent allowed quantifying its continuity index. Solvents have to be carefully chosen to dissolve or extract completely each phase without any influence on the second one. In this study, PBSA was dissolved in dichloromethane (99.9%, Chimie Plus, Denice, France) during 24 h whereas PLS was hydrolyzed in 6 mol L⁻¹ HCl during 48 h (Sarazin, Li, Orts, & Favis, 2008; Schwach & Avérous, 2004). The extraction

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