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Influence of transesterification reactions on the miscibility and thermal properties of poly(butylene/diethylene succinate) copolymers

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ABSTRACT

Poly(butylene/diethylene succinate) block copolymers (PBSPDGS), prepared by reactive blending of the parent homopolymers (PBS and PDGS) in the presence of $Ti(OBu)_4$, were analyzed by ^{1}H-NMR, TGA and DSC, in order to investigate the effects of the transesterification reactions on the molecular structure and thermal properties. ^{1}H-NMR analysis evidenced the formation of copolymers whose degree of randomness increases with the mixing time. The thermal analysis of the melt-quenched samples showed that the melting peak, due to the crystalline phase of PBS, tends to disappear with increasing mixing time and therefore with decreasing the block length in the copolymers. As concern miscibility, a single homogeneous amorphous phase always occurred, independently on block length. Nevertheless, a phase separation, due to the tendency of the PBS blocks to crystallize, was evidenced in the copolymers with long butylene succinate sequences. The results obtained indicated that the block size had a fundamental role in determining the crystallizability and, therefore, phase behavior of the block copolymers.

1. Introduction

In recent years, increased concern about environmental impact of human lifestyle has fuelled research for the development of biodegradable polymers. These latter have been also extensively used in biomedical applications, for example as biomaterials for constructing absorbable bone plates and other surgical fixation devices, surgical sutures, controlled release drug carriers, etc. [1–3]. The biocompatibility, toxicity, and immunogenicity of polymers play important role in these applications; other relevant factors concern a predictable rate of biodegradation and deliverable mechanical properties.

In this view, aliphatic polyesters have been attracting considerable attention as they combine the features of biodegradability and biocompatibility with physical and chemical properties comparable with some of the most extensively used polymers, like LDPE, PP, etc. Moreover, they can be processed into various forms, such as fibers, films and injection-moulded devices [1–3]. Commercial aliphatic polyesters are produced mainly through condensation polymerization of aliphatic dicarboxylic acids with diols, transesterification reaction of diesters with diols, polymerization of hydroxy acids and ring-opening polymerization of lactones [4].

Poly(butylene succinate) (PBS) is an important member of aliphatic polyester family, having physical properties similar to those of PE. PBS and related copolymers have shown considerable promises for uses as environmentally biodegradable thermoplastics, as well as bioabsorbable/biocompatible medical materials.

Polymer blending is an effective way of achieving a deliverable combination of properties, which are often absent in single component polymers. However, a polymer blend is often characterized by poor mechanical properties as many polymers are thermodynamically immiscible. Upon melt processing at sufficiently high temperatures, it

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is known that polyester blends may undergo transesterification or in general exchange reactions, accelerated by the catalyst residues in the polyesters. These reactions can lead to the formation of block/random copolyesters from the original binary pair. The resulting block or random copolymers, owing to transesterification, are expected to exhibit better mutual miscibility than the original unreacted components [5]. This means that when polyester blends are held at high temperatures, i.e. above their melting points, an interchange reaction can occur among the component polyesters, leading eventually to exchanged copolyesters of various sequences/block. Recently, Marchese et al. showed that the exchange reactions depend strongly on the initial compatibility between the two polymers and on the blending conditions, i.e. mixing temperature and time, apparatus used, viscosity match, and presence of catalysts and inhibitors [6]. It has to be emphasized that an accurate control of the blending conditions is crucial for obtaining materials with predetermined properties.

Recently, Cao et al. synthesized random poly(butylene/diethylene succinate) copolymers and investigated their thermal and mechanical properties with the aim of correlating them to composition [7]. It is noteworthy that poly(diethylene succinate) (PDGS) differs from PBS because of the introduction ether-oxygen atoms along the PBS chains. There is a great current interest on polyesters based on alkylene ether glycols: the presence of ether linkages in the chain seems indeed to increase the hydrophilic character of the polymer, favouring its dissolution under environmental conditions and/or enhancing the affinity with living cells [8,9]. This latter aspect is very important because it can be correlated with the capacity of some polymeric biomaterials to favour the regeneration of tissues through their interaction with the cells. Hence, surgical implants made from biomaterials could be used as a temporary scaffold in tissue engineering.

Taking into account that this approach toward the reconstruction of injured, diseased, or aged tissues is one of the most promising fields in the 21st century, it appears interesting to prepare novel biocompatible and biodegradable block copolymers based on PBS and PDGS by reactive blending. A detailed investigation of their thermal properties and miscibility has been carried out and the results are reported in the present paper.

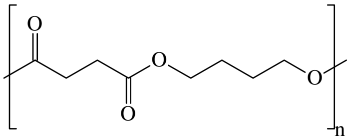
2. Experimental

2.1. Products

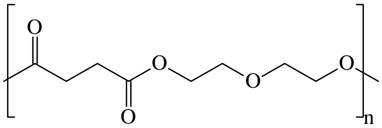
Dimethylsuccinate (DMS), 1,4-butanediol (BD), diethylene glycol (DEG), and titanium tetrabutoxide ($Ti(OBu)_4$) (Aldrich) were reagent grade products; DMS and BD were used as supplied, whereas DEG and $Ti(OBu)_4$ were distilled before use.

2.2. Synthesis of homopolymers

Poly(butylene succinate) (PBS) and poly(diethylene succinate) (PDGS) were synthesized in bulk starting from dimethylsuccinate and the appropriate glycol in a molar ratio 1:2, employing $Ti(OBu)_4$ as catalyst (about 0.2 g of $Ti(OBu)_4$/kg of polymer). The syntheses were carried out in a 500 mL stirred glass reactor, with a thermostatted silicon oil bath; temperature and torque were continuously recorded during the polymerization. The polymers were prepared according to the usual two-stage polymerization procedure. In the first stage, under pure nitrogen flow, the temperature was raised to 180 °C and maintained there for until more than 90% of the theoretical amount of methanol was distilled off (about 2 h). In the second stage the pressure was reduced (about 0.1 mbar), in order to facilitate the removal of the glycol in excess and the temperature was kept at 210°; the polymerization was carried out until a torque constant value was measured. The chemical structures of the two homopolymers synthesized are the following:



PBS



PDGS

2.3. Synthesis of poly(butylene/diethylene succinate) copolyesters

Poly(butylene/diethylene succinate) copolyesters were obtained by melt mixing of PBS and PDGS. The two homopolymers were mixed in a 1:1 molar ratio in a 200-mL glass reactor at 225 °C under nitrogen atmosphere to prevent hydrolytic degradation. During the process, samples were taken from the reactor at different reaction times (5, 15, 30, 45, 60, 90 and 120 min) and cooled in air. Copolymer formation is catalyzed by the residual titanium tetrabutoxide, introduced in the polymerization of PBS and PDGS. The copolyesters obtained and analyzed in this work will be indicated with PBSPDGSX, where X is the mixing time.

2.4. ^{1}H-NMR spectroscopy

The polymer structure and composition were determined by means of ^{1}H-NMR spectroscopy. The samples were dissolved (15 mg/mL) in chloroform-*d* solvent with 0.03% (v/v) tetramethylsilane added as an internal standard. The measurements were carried out at room temperature, employing a Varian INOVA 400 MHz instrument.

2.5. Gel-permeation chromatography

Molecular weight data were obtained by gel-permeation chromatography at 30 °C using a 1100 Hewlett Packard system equipped with PL gel 5μ MiniMIX-C column (250/4.6 length/i.d., in mm). A refractive index was