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Material Properties

Thermal behavior, mechanical and rheological properties, and hydrolytic degradation of novel branched biodegradable poly(ethylene succinate) copolymers



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ABSTRACT

The thermal behavior, mechanical and rheological properties, and hydrolytic degradation of novel branched biodegradable poly(ethylene succinate) (PES) copolymers were studied in detail and compared with those of linear PES. The branched copolymers displayed the same crystal structure as the linear homopolymer. The glass transition temperature, melting point and heat of fusion of branched PES copolymers were lower than those of linear PES and further decreased gradually with an increase of side chain content. The dynamic storage modulus values of branched PES copolymers were less than that of linear PES, and also decreased with increasing side chain content. All samples behaved as non-Newtonian fluids. Furthermore, the dynamic complex viscosity, loss modulus and storage modulus exhibited a decreasing tendency with increasing side chain content at all frequency ranges studied. In addition, the hydrolytic degradation rates were slower in branched PES copolymers than in linear PES.

1. Introduction

Biodegradable polymers have recently attracted considerable research interest from both academic and practical viewpoints [1–6]. Poly(ethylene succinate) (PES) is an important member of biodegradable aliphatic polyesters, as its monomer of succinic acid may be derived from natural resources. PES has comparable physical properties to those of some traditional thermoplastics like polyethylene and polypropylene and, therefore, has been extensively studied in literature [7–12]. Some polymers have been used to prepare PES based polymer blends to improve the physical properties for a wider practical application; however, polymer blending may face the problem of phase separation which, in turn, affects the physical properties of the blends [13–15]. In addition to physical polymer blending, copolymerization has also often been used to provide an effective way to modify PES incorporating another component into the molecular chain. A series of PES based copolymers has already been synthesized by the incorporation of some third comonomers (diols or diacids), such as poly(ethylene succinate-*co*-propylene succinate), poly(ethylene succinate-*co*-butylene succinate), poly(ethylene succinate-*co*-octamethylene succinate), poly(ethylene succinate-*co*-decamethylene succinate), poly(ethylene succinate-*co*-ethylene adipate), and poly(ethylene succinate-*co*-ethylene suberate) [16–23]. The crystal structure, crystallization kinetics,

crystalline morphology, thermal and mechanical properties, and hydrolytic degradation behavior of these PES based copolymers have been intensively investigated. It should be noted that these PES based copolymers are all linear aliphatic polyesters, therefore, the comonomer unit should reside along the main chain of PES.

Branched polymers or polymers with side chains may offer another way to make modifications [24]. For example, the processability and mechanical properties of polyethylene could be well regulated by introducing side chains or long chain branching [24–29]. In addition, biodegradable aliphatic polyesters with side chains have also been studied in recent years [30–33]. The side chains may behave differently as a diluent, a plasticizer or a nucleating agent, depending on the type and content of side chains. Jin et al. introduced *n*-hexenyl side branches into poly(butylene succinate) (PBS) backbone and found that the synthesized branched PBS copolymers showed improved biodegradability and decreased glass transition temperature and melting temperature, compared with those of PBS [30]. Chae et al. prepared branched PBS copolymers with methyl side branches and studied the effect of methyl substitution on the properties of PBS [31]. Jin et al. studied the effect of *n*-octyl as well as ethyl branches on the properties of poly(ethylene adipate) (PEA) [32,33]. They reported that the biodegradation properties were improved, while the melt viscosity and the toughness of branched PEA decreased with the introduction of *n*-octyl branches and

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ethyl branches. Some long chain branching copolymers based on aliphatic polyesters have also been studied recently; the rheological and mechanical properties and degradation behavior could be well regulated [34–36].

To our knowledge, branched PES based copolymers have not been reported so far. Branched PES based polymers should show some different physical properties from the linear PES homopolymer, as a certain amount of side chains are connected with the main backbone of PES through chemical bonds. Therefore, we first synthesized two branched PES copolymers with low contents of *n*-octyl pendant groups as side chains and investigated their crystal structure, basic thermal behavior, mechanical and rheological properties, and hydrolytic degradation, and compared them with linear PES homopolymer.

2. Experimental

2.1. Materials

Ethylene glycol was purchased from Beijing Chemical Works. 1,2-decanediol was bought from TCI (Shanghai) Development Co., Ltd. Succinic acid was purchased from Tianjin Fuchen Chemical Reagents Factory. Tetrabutyl titanate was bought from Beijing Chang Ping Jing Xiang Chemical Factory. All reagents were directly used without further purification.

2.2. Synthesis of branched PES based copolymers and linear PES

The novel branched PES copolymers with about 5 and 10 mol% of side chains were synthesized via a two-step melt condensation process by using 1,2-decanediol as a new comonomer. The determined amount of monomers (ethylene glycol, succinic acid, and 1,2-decanediol) were first added into a three-necked flask (the molar percent of diacid/diol was 1:1.1). The catalyst tetrabutyl titanate with 0.1 mol% of succinic acid was added simultaneously. The reactants were then heated to 150 °C and held until they were completely melted under nitrogen atmosphere. They were further gradually heated to 190 °C and held for 2–3 h. The reaction temperature was then gradually increased to 230 °C during the polycondensation process under a low pressure of about 400 Pa for almost 4 h. The reaction was stopped when the speed of the stirring paddle sharply slowed down. The same synthesis procedure was also used to prepare linear PES. The products obtained were dissolved in chloroform and precipitated by methanol several times. The samples were dried under vacuum at 30 °C for 3 days to remove any residual solvents.

2.3. Characterization

The compositions of the synthesized branched PES copolymers were determined by hydrogen nuclear magnetic resonance (¹H NMR) on a Bruker AV 600 spectrometer using deuterated chloroform (CDCl₃) as the solvent.

The weight average molecular weight (M_w) and polydispersity index (PDI) of the branched PES copolymers and linear PES were measured by gel permeation chromatography (GPC) (Waters Company, USA) using chloroform as a solvent.

The wide-angle X-ray diffraction (WAXD) experiments were performed on a Rigaku d/Max2500 VB2 +/PC X-ray diffractometer from 5° to 45° at 4°/min. The samples were first annealed at 140 °C for 3 min to erase any thermal history, then pressed into around 1 mm thick films, and finally crystallized at 54 °C for 12 h in a vacuum oven.

The basic thermal properties of the branched PES copolymers and linear PES were studied with a TA Instruments Q100 differential scanning calorimeter (DSC). The samples were first annealed at 140 °C for 3 min to erase any previous thermal history and then quenched to –80 °C at 60 °C/min to reach the completely amorphous state. The thermal properties of the samples were studied with DSC from the

amorphous state at a heating rate of 10 °C/min.

The dynamic mechanical analysis (DMA) tests of the branched PES copolymers and linear PES were performed on a Netzsch 242C dynamic mechanical analyzer. The experiments were conducted under tension film mode within the temperature range of –100 to 80 °C at a frequency of 1 Hz at a heating rate of 3 °C/min. The samples for the DMA experiments were molded and cut into films with dimensions of 10 × 5 × 1 mm.

The rheological behavior of the branched PES copolymers and linear PES was studied on a strain-controlled rheometer (Anton Paar, MCR301) using parallel plates at 130 °C. Small-amplitude oscillatory shear ($\gamma = 1\%$) measurements were performed within a frequency range from 0.3 to 500 rad/s. The sample disks were prepared by compression molding into parallel plates with a diameter of 25 mm and a thickness of 1 mm.

The hydrolytic degradation of the branched PES copolymers and linear PES was investigated in sodium hydroxide (NaOH) solution of pH = 14 at 37 °C for different periods of time. The samples were first molded and cut into small size specimens (about 100 mg). After the hydrolytic degradation, the specimens were washed with deionized water and further dried for enough time to reach constant weight. The weight loss (W_{loss}) was calculated through the following equation:

$$W_{\text{loss}} (\%) = 100 \times (W_0 - W_t)/W_0 \quad (1)$$

where W_0 is the initial weight and W_t is the weight of sample subjected to hydrolytic degradation for time t . The hydrolytic degradation rate was derived from the slope of the plot of weight loss versus hydrolytic degradation time.

3. Results and discussion

3.1. Composition and molecular weight of branched PES

The chemical structure of branched PES copolymers is illustrated in Fig. 1. The ¹H NMR spectrum of the branched PES copolymer containing around 10 mol% of 1,2-decamethylene succinate (DS) unit is also displayed in Fig. 1, from which the exact composition of the copolymer may be determined. As depicted in Fig. 1, the characteristic resonance signal *a* at 4.30 ppm was ascribed to the methylene protons of ethylene glycol. The signal *b* at 2.67 ppm was caused by the protons of succinic acid. Those characteristic resonance signals at 5.08 and 0.88 ppm were denoted as the *d* and *g* of 1,2-decanediol, respectively. Those characteristic resonance signals *c* and *c'* at 4.24 and 4.07 ppm and the ones *e* and *f* at 1.60 and 1.25 ppm were all caused by the protons of 1,2-decanediol [36]. In the present work, the exact composition of the copolymer was determined on the basis of the ratio of the intensity of the signal *g* corresponding to the DS unit to that of the signal *a* corresponding to the ethylene succinate (ES) unit. The results are listed in Table 1. From Table 1, the exact compositions of the synthesized copolymers were close to the feed compositions, indicating successful synthesis of the branched PES copolymers. For brevity, the samples with the DS contents of 4.6 and 9.6 mol% were designated as PED5S and PED10S, respectively.

As the physical properties and biodegradation behavior of biodegradable polymers are dependent on their molecular weight, the M_w and PDI values of linear PES and its branched copolymers were first measured with GPC, and are summarized in Table 1 for comparison [37]. From Table 1, the branched and linear PES samples showed relatively high M_w values; moreover, the M_w and PDI values of all the three samples were close to each other, regardless of the branching degree. Therefore, the influence of M_w on the thermal, mechanical, and rheological properties and hydrolytic degradation of the branched and linear PES samples should be relatively little.

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