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Crystallization and melting of biodegradable poly(propylene suberate)

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ABSTRACT

Thermal behavior of poly(propylene suberate) (PPSub) was studied. PPSub is a novel biodegradable polyester which always shows lower crystallinity, and thus faster biodegradation, than poly(ε-caprolactone) or poly(butylene succinate). Crystalline structure, multiple melting behavior and re-crystallization of PPSub on heating were studied by using Wide Angle X-ray Diffraction (WAXD), Differential Scanning Calorimetry (DSC) and Step Scan DSC. The equilibrium melting point and the enthalpy of fusion of the pure crystalline polymer were found 79.7 °C and 28.9 kJ/mol, respectively. Polarized Light Microscopy (PLM) tests showed that PPSub forms banded spherulites. The Lauritzen–Hoffman theory was used. Values of spherulite growth rates and also overall crystallization rates after self-nucleation, from DSC data, were used. In the latter case the inverse of crystallization half times or the Avrami constant *K* values were supposed to be a measure of crystallization rates. Critical breakpoint in the Lauritzen–Hoffman plots appeared at 40 °C showing crystallization regime II to III transition. Non-isothermal crystallization kinetics was also analyzed. Interestingly, the Ozawa model seems to hold for PPSub. The iso-conversional method of Friedman was used to study the activation energy of PPSub crystallization on cooling and the Lauritzen–Hoffman parameters were also calculated by applying the Vyazovkin method.

1. Introduction

Biodegradable and biocompatible polymers have attracted significant attention in the last decades. They are environmental friendly, as they degrade under the action of physicochemical and biological factors in a humid environment, while they can be employed in many biomedical and pharmaceutical applications such as sutures, implant materials and materials for tissue engineering and biologically active controlled-release devices [1–3]. An important class of biodegradable polymers is that of aliphatic polyesters, which are degradable hydrolytically or enzymatically. Biodegradable polyesters may occur naturally (i.e. PHB, cutin, suberin, and estolide) they can be synthesized from petrochemicals (i.e. PCL and PBS) and can as well be derived from renewable resources (i.e. PLA and PHB) [4].

Over the past few years, most of the effort in making aliphatic polyesters has been focused on 1,4-butandiol and very little emphasis has been given to 1,3-propanediol. This was because there were difficulties in industrial scale production of high purity 1,3-propanediol (1,3-PD) [5,6]. However, new and more attractive processes have been developed for the production of 1,3-propanediol (1,3-PD) from renewable resources. Thus research on related polymers has attracted interest from both industrial and academic viewpoint [7,8]. As a matter of fact polyesters of 1,3-PD show excellent properties. For example, poly(propylene terephthalate) (PPT) [or poly(trimethylene terephthalate) (PTT)], the first and most studied polyester of 1,3-propanediol, is already commercially available [9,10]. Due to the even number of methylene groups of the diol segment, PPT chains can be stretched up to 15% with a reversible recovery [11]. In practice PPT fibers are characterized by much better resilience and stress/recovery properties than poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT). Unfortunately, like the other terephthalate polyesters, PPT is not susceptible to degradation in environment.

Poly(propylene succinate) was the first biodegradable polyester from 1,3-PD that was studied [12–14]. Synthesis and characterization of a series of biodegradable polyesters of 1,3-propanediol and different dicarboxylic aliphatic acids containing from 2 up to 8 methylene groups between their carboxyl groups were reported only in two recent publications [15,16].

Solid state characteristics of a polymer specimen are reflected on its thermal behavior [17]. Thus, multiple melting endotherms in differential scanning calorimeter (DSC) traces of semicrystalline polymers are often observed [17–24]. The most common concepts concerning multiple melting behaviors of polymers are the melting of crystals of different stability (dual morphology mechanism) and the melting, recrystallization, remelting process (reorganization mechanism) [25,26]. Modulated temperature DSC techniques are

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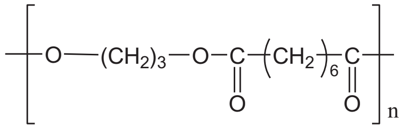
appropriate to distinguish endothermic phenomena like melting, from exothermic ones like re-crystallization [27–31]. Visualization of the effect of re-crystallization can be easier achieved using High Rate DSC or thin film (chip) calorimetry [32,33].

Crystallization is crucial for the optimization of the processing conditions and the properties of the end product especially for fast crystallizing biodegradable polymers [34]. Overall crystallization rates under isothermal conditions are generally analyzed with the use of the so-called Avrami equation [35–40]. Also, the secondary nucleation theory of Lauritzen–Hofmann is often used for the analysis of the sherulitic growth rates under isothermal conditions. However, although isothermal data allow theoretical analysis of crystallization, solidification during polymer processing is always dynamic. In fact, non-isothermal crystallization of polymers is quite difficult to be modelled, but some authors assumed it can be approximated by a sequence of infinitesimally small isothermal stages, so it can be described by modifications of the Avrami equation [41].

To our knowledge, poly(propylene suberate) has only been reported in a single paper [15]. Details of the thermal behavior of the polyester have never been reported before. On the other hand previous studies of enzymatic degradation and also mechanical properties of the polymer showed a very interesting behavior. In fact poly(propylene alkane-dicarboxylate)s have faster biodegradation among the studied aliphatic polyesters chemically synthesized and the particular polymer PPSub shows the faster rates among all [15]. The point is that in general PPSub behaves similarly to PCL or PBSu, while it shows slower crystallization and faster biodegradation than these well known biodegradable polymers. This means that PPSub might be a potential candidate for applications especially in medicine or pharmaceutical technology. Melting and crystallization studies offer significant information in order to fully characterize the material and better understand the specifications prior to exploit the advantages offered in applications. Also, detailed studies in comparison to other polymers allow for the understanding of specific aspects of the crystallization or melting of polymers and thus the improvement of processing techniques. Thus, in this paper a detailed study of the melting and crystallization behavior of poly(propylene suberate) (**I**) is presented in comparison to other biodegradable polyesters.



$$\left[-O-(CH_2)_3-O-\underset{\substack{\|\\ O}}{C}-(CH_2)_6-\underset{\substack{\|\\ O}}{C}-\right]_n$$

(I)

2. Experimental

2.1. Materials

Poly(propylene suberate) was synthesized from Suberic acid and 1,3-propanediol (1,3-PD). Suberic acid (purum 99%) was purchased from Aldrich Chemical Co. 1,3-Propanediol (CAS Number: 504-63-2, purity: >99.7%) was kindly supplied by Du Pont de Nemours Co. Tetrabutyl titanate catalyst of analytical grade and polyphosphoric acid (PPA) used as heat stabilizer were purchased from Aldrich Chemical Co. All the other materials and solvents which were used for the analytical methods were of analytical grade.

Poly(propylene suberate) sample was prepared by the two-stage melt polycondensation method (esterification and polycondensation) in a glass batch reactor following the well-known method for polyester preparation [15]. In brief, the proper amount of suberic acid and 1,3-propanediol in a acid/diol molar ratio 1/1.1 and the catalyst $Ti(OBu)_4$ were charged into the reaction tube of the polyesterification apparatus. The apparatus with the reagents was evacuated several times and filled with argon in order to remove the whole oxygen amount. The reaction mixture was heated at 180 °C under argon atmosphere and stirring at a constant speed (500 rpm).

In the second step of polycondensation, PPA was added (5×10^{-4} mol PPA/mol suberic acid), which is believed that prevents side reactions such as etherification and thermal decomposition. A vacuum (5.0 Pa) was applied slowly over a period of time of about 30 min, to avoid excessive foaming and to minimize oligomer sublimation, which is a potential problem during the melt polycondensation. The temperature was slowly increased to 230 °C while stirring speed was increased at 720 rpm. The polycondensation continued for about 60 min.

2.2. Characterization

2.2.1. Intrinsic viscosity measurement

Intrinsic viscosity measurements were performed using an Ubbelohde viscometer Oc at 25 °C in chloroform, at a solution concentration of 1 wt%. The intrinsic viscosity of the sample was found to be 0.607 dL/g.

2.2.2. Gel permeation chromatography (GPC)

GPC analysis was performed using a Waters 150C GPC equipped with differential refractometer as detector and three ultrastyragel (10^3, 10^4, 10^5 Å) columns in series. $CHCl_3$ was used as the eluent (1 mL/min) and the measurements were performed at 35 °C. Calibration was performed using polystyrene standards with a narrow molecular weight distribution. Results showed that the number average molecular weight (M_n) of PPSub was equal to 15,000 Da with polydispersity $M_w/M_n = 2.09$.

2.2.3. Differential Scanning Calorimetry (DSC)

A Perkin-Elmer, Pyris Diamond differential scanning calorimeter (DSC), calibrated with Indium and Zinc and Cyclohexane standards, was used for the study of crystallization and melting of the polyesters. Samples of 5 ± 0.1 mg were used in tests. They were sealed in aluminium pans and heated at a heating rate 20 °C/min to 100 °C, which is about 40 °C above the end of melting and quite above the equilibrium melting point of the polymer. The samples were held at 100 °C for 3 min in order to erase any thermal history. For isothermal crystallizations the sample was rapidly cooled to 20 °C above the crystallization temperature and finally cooled to that at a rate 50 °C/min, to achieve equilibration of the instrument. The crystallization exothermic peak was then recorded. Heating scans were performed at a rate of 20 °C/min. If some other procedure was followed in specific tests this will be described in the corresponding part.

Isothermal crystallization experiments were also performed after self-nucleation of the polyester sample. Self-nucleation measurements were performed in analogy to the procedure described by Fillon et al. and Müller et al. [42–44].

The protocol used is very similar with that described by Müller et al. [43] and can be summarized as follows: (1) melting of the sample at 100 °C for 3 min in order to erase any previous thermal history; (2) subsequent cooling at a rate of 10 °C/min to 0 °C, which creates a "standard" thermal history; (3) partial melting by heating at 10 °C/min up to a "self-nucleation temperature", T_s; (4) thermal conditioning at T_s for 5 min. Depending on T_s, the crystalline polyester domains will be completely molten, only self-nucleated or self-nucleated and annealed. If T_s is sufficiently high, no self-nuclei or crystal fragments can remain and the sample is then in the so-called Domain I, the complete melting domain. At intermediate T_s values, the sample is almost completely molten, but some small crystal fragments or crystal memory effects remain, which can act