



Modulated crystallization behavior, polymorphic crystalline structure and enzymatic degradation of poly(butylene adipate): Effects of layered metal phosphonate

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ABSTRACT

Layered metal phosphonate, zinc phenylphosphonate (PPZn) was synthesized and used as a model benign nucleating agent for poly(butylene adipate) (PBA) to manipulate the crystallization behavior, polymorphic crystalline structure and biodegradation of PBA. Upon incorporation of PPZn, the crystallization temperature (T_c) and crystallinity of PBA increased. Meanwhile, the crystallization rate and spherulite density of PBA increased in the presence of PPZn, indicating that PPZn has an effective nucleating effect for PBA. PPZn is favorable for the formation of the PBA α -modification. Furthermore, PPZn would speed up highly the phase transition of PBA from the β - to α -one. PPZn significantly suppressed the biodegradation of PBA. Mechanisms for nucleating, preferential formation of the α -modification, accelerated phase transition and decreased degradation rate of PBA in the presence of PPZn have also been proposed. It is considered that layered metal phosphonate material is a new type of benign filler for controlling the polymorphic crystalline structure and biodegradation rate of the polymer, which is expected to further modify the property of the polymer and might widen the applications of biodegradable materials in the environmental and biomedical fields.

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1. Introduction

Poly(butylene adipate) (PBA), a typical linear aliphatic polyester, can be potentially used in biomedical and eco-friendly materials for its biodegradability [1–5]. Recently, much attention has been paid on PBA due to the complicated and interesting relationship among its polymorphic crystalline structure (aggregation structure), crystallization rate, multiple thermal melting behavior, morphology, biodegradability. Depending on the melt–crystallization temperature (T_c), PBA can crystallize into the α modification ($T_c > 32$ °C), β modification ($T_c < 29$ °C), and the mixture of α and β modification ($(\alpha + \beta)$, 29 °C $\leq T_c \leq 32$ °C) [6–14]. The crystallization rate of the β modification is faster than that of α one. The α modification can be characterized as the monoclinic unit cell and β one as orthorhombic unit cell [15,16]. Both the α and β modifications present the Maltese-cross ringless spherulites (the size of the α spherulite is larger than that of the β one), but the $(\alpha + \beta)$ mixture shows the ring-band

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spherulite [6–8]. The multiple melting points (T_m) have been reported for both the α and β modifications, but T_m of the β modification is relatively higher than that of α one, attributable for the additional energy used for the phase transition from the β crystal to α one during the heating process of the β crystal [7]. Therefore, the α -modification is the so-called thermodynamically stable phase and the β one is metastable phase [7]. It is noted that the α -modification (with the larger crystal size, higher crystallinity and thermal stability) shows the faster biodegradation rate than the β one (with the smaller crystal size, lower crystallinity and thermal stability), which is contrary to the general expectation. It is of particular interest that, the ($\alpha + \beta$) mixture with the ring-band spherulite shows the lowest biodegradation rate, which is even lower than that of the β modification [8].

It is well known that the properties (such as thermal stability, mechanical property, biodegradability, transparency, and gas barrier property) of the polymer are strongly related to its morphology and polymorphic crystalline structure (aggregation structure). Hence it is reasonable to tailor the biodegradability and thermal stability of PBA via manipulating its spherulite morphology and polymorphic crystalline structure. Up to date, many factors have been found to influence the polymorphic crystalline structure and morphology of PBA, such as fractionation [17], nucleating agent (NA) [13,14,18–26], comonomer [27], fusion temperature prior to crystallization [11], epitaxial crystallization [28,29], blending [2–4,30–32], stretching and molecular weight [33] and stress-dependent polymorphism in several block copolymer [34–36].

In general, two important stages, that is, nucleating and crystal growth are involved in the crystallization process of the polymer. A primary nucleation process can occur in two conditions. The first is homogeneous nucleation that is not affected in any way by solids. The second one is heterogeneous nucleation resulting from solid particles of foreign substances (or impurities), which leading to the enhancement in the rate of nucleation. It should be noted that it is more difficult for homogeneous nucleation compared to heterogeneous one (especially at low supercooling) due to the necessary high energy used for initiating the nucleation without a solid surface which would catalyze the nucleation. The heterogeneous nucleation can occur at low supercooling due to the presence of foreign substances in the polymer melt which would increase the crystallization rate by serving as heterogeneous nuclei and decrease the free energy for the formation of a critical nucleus [37,38]. These added foreign substances showing high performances in the acceleration of the nucleation are the so-called NAs.

Chemical modification [27,33] (such as, preparation of the copolymer and increasing the molecular weight) maybe a useful approach to manipulate the crystallization rate and/or crystal modification of PBA, but is complicated, high cost, and not time saving. Blending is a widely spread way to tailor the performances of the polymer because of its simpleness, effective, low-cost and convenience. Strictly speaking, addition of NA is also considered as the same way to the blending. However, incorporation of small amount of NA (1%) significantly manipulate the polymorphic crystalline structure and biodegradability of PBA [13,14,18,19]. Thus, with respect to effectiveness and economy, the NA is probably more useful substance in tailoring the microstructure and performance of the polymer. Until now, some NAs have been developed and used in the scientific research, as mentioned above. However, the biodegradability and biocompatibility of several NAs are still unclear.

Recently, a kind of synthetic inorganic/organic hybrid material with a layered structure, metal phosphonate, has attracted much attention as a new kind of benign filler. Upon addition of layered metal phosphonates (e.g., α -zirconium phosphate), the mechanical properties and thermal stability of polymers, for example, epoxy [39,40], poly(acrylamide) [41], and poly(ethylene terephthalate) (PET) [42] can be manipulated. The applications of metal phosphonate in chemical sensor [43], sorbents [44], catalyst [45], and ion exchange [46] have also been witnessed. In addition, the metal phosphonate can also be utilized as biomaterials because phosphate is a naturally occurring functional group. It has been documented [47] that calcium phosphate is a potential implant for bone reconstruction. It has been also reported [48] that metal phosphonates can be applied in oligonucleotide microarrays, protein binding, and drug-delivery systems. Herschke et al. [49] suggested that zinc phosphate is a versatile material for potential biomedical application, such as bone replacement cements. Especially, via altering the types of metal ions or organic group, the properties of metal phosphonates could be modulated.

In the previous report [38], zinc phenylphosphonate (PPZn) was selected as a kind of benign NA to accelerate the crystallization of poly(L-lactide), and increase its tensile and storage modulus. In this work, PPZn, a model metal phosphonate was used as NA incorporated into the PBA to investigate its effect on the crystallization behavior, polymorphic crystalline structure, phase transition and biodegradation of PBA. The non-isothermal behavior and isothermal crystallization kinetics, spherulite morphology, polymorphism and enzyme biodegradation of PBA were examined by differential scanning calorimetry (DSC), polarized optical microscopy (POM), wide angle X-ray diffraction (WAXD), and Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). The mechanism of PPZn on the nucleation, control of the polymorphism and enzymatic degradation of PBA were also proposed. To the best of our knowledge, this work is firstly reported on the crystallization behavior, polymorphism and property (biodegradation) of PBA, which was investigated systematically and thoroughly via addition of a biocompatible (benign) and model NA (PPZn). It will shed a light to adjust the polymorphic crystalline structure and property of the polyester via epitaxial growth of the polyester on the surface of green filler/NA.

2. Experimental section

2.1. Materials

PBA ($M_w = 12,000$ Da) was purchased from Sigma–Aldrich Co. Before use, PBA was purified by precipitating into ethanol from the chloroform solution and then was dried under vacuum at 40 °C for 1 week. $ZnCl_2$, phenylphosphonic acid, and NaOH, which are all analytical grade, were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan) and used as received.

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