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Synthesis of Poly(butylene succinate) phosphorus-containing ionomers for versatile crystallization and improved thermal conductivity

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HIGHLIGHTS

- Poly(butylene succinate) phosphorus-containing ionomers (PBSIs-K) are synthesized by condensation polymerization.
- A small amount of PCI groups for PBSIs-K can facilitate the crystallization.
- The thermal conductivity and spherulitic diameter of PBSI1-K are promoted from 110 to 320 mW/m.k and 181 to 353 μm.
- A brittle-ductile transition for PBSIs-K can be observed when the PCIG content increases from 2.6% to 5.2%.

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ABSTRACT

To explore the relationship between crystallization and properties of biodegradable ionomers for improving comprehensive performances, poly(butylene succinate) phosphorus-containing ionomers (PBSIs-K) with different ionic group content were synthesized by condensation polymerization of succinic acid, 1,4-butanediol and phosphorous ion monomers (DHPPO-K). The chemical structures, experimental phosphorus content and intrinsic viscosities of PBSIs-K were determined by ^{1}H and ^{31}P NMR spectroscopy, inductively coupled plasma optical emission spectrometry and Ubbelohde viscometer, respectively. The effects of phosphorus-containing ionic group (PCIG) content on the thermal behavior, crystallization, rheological behavior of PBSIs-K were investigated by differential scanning calorimeter, polarizing optical microscopy, X-ray diffraction, rotational rheometer and dynamic mechanical analysis, respectively. They revealed that the crystallinity, grain diameter and spherulitic diameter of PBSIs-K initially increased and then reduced with the increase of PCIG content. The shear viscosity and T_g of PBSI7.5-K (7.5%PCIG content) increased due to physical crosslinking by ionic aggregates. Then the thermal conductivity, mechanical properties, hydrolytic degradation and gas barrier property of PBSIs-K were evaluated. The thermal conductivity of PBSI1-K (1%PCIG content) was strikingly promoted from 110 to 320 mW/m·k as the spherulitic diameter increased from 181 to 353 μm. Noteworthy, the elongation at breakage of PBSI7.5-K increased from 37% to 529% and the brittle-ductile transition was assigned to significant variations for PBSI7.5-K crystallization. Furthermore, hydrolytic degradation rate of PBSIs-K was dominated by PCIG content and was drastically accelerated when PCIG content ranged from 3% to 5%. The study revealed that the properties of PBSIs-K were dependent on PCIG content and provided a promising approach for biodegradable PBSI fabrication with versatile properties.

1. Introduction

In recent decades, biodegradable materials have attracted tremendous attention due to their development sustainable and environment benign [1]. Among them, Poly(butylene succinate) (PBS) is a type of fully biodegradable and biocompatible semi-crystalline aliphatic polyesters with excellent mechanical properties, good heat resistance and processability, used for numerous applications such as packaging materials, agricultural film and biomedicine since the first research in the 1990s [2–8]. The presence of linear molecular chain structure leads the intermolecular action of PBS to be dominated by Van der Waals force. Thus, the most noticeable properties for PBS is employed as semi-crystalline and low melt strength, simultaneously. Consequently, the applications of PBS are restricted in the films and foams by its low

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ductility and poor thermal processing.

Ionization for PBS, differs with those traditional chemical or physical modification methods, such as copolymerization, blending or compounding [9–15], has recently attracted a great deal of attention [16–24]. Due to aggregation of ionic groups, physical cross-linking sites could be formed. As ionic group concentration grew higher, the physical cross-linking sites hindered chain mobility by clusters consisting of numerous multiplets [25,26]. Therefore, the introduction of versatile ionic groups into PBS can significantly promote the increases in the melt strength, crystallization rate, hydrolytic degradation rate, mechanical properties and other properties [27–32]. Recently, ionomers have been utilized in several commercial fields including foams [33], fibers, conducting materials, shape memory polymers, self-healing materials and so on [34–36].

Among ionomers, the ionic groups such as sulfonated, are incorporated to the hydrophobic polymer chains as pendant moieties. The performances of ionomers are sensitive to variations in the molar fraction (usually less than 15 mol %) and type of ionic groups. Han et al. [14] have analyzed the crystallization behavior of a poly(butylene succinate)-based ionomer (PBSi) containing dimethyl 5-sulfoisophthalate sodium salt (DMSI). The result indicated that the presence of ion aggregates and benzene groups affects the extent of diffusion of chains towards crystallization. Similarly, Lv et al. [15] used DMSI to synthesize high molecular weight poly(butylene succinate) ionomers (PBSIs) with controlled ionic group distributions via chain extending. All the results revealed that the properties of PBSI can be regulated by the ionic group distribution. Zeng et al. [37] found that the incorporation of urethane segments containing secondary amine cation to poly(ethylene succinate) (PES) chains could considerably accelerate the crystallization rates of PES due to the improved nucleation efficiency. Wu et al. [26] synthesized segmented poly(butylene succinate) urethane ionenes by chain extension reaction of dihydroxyl terminated poly (butylene succinate) and diethanolamine hydrochloride (DEAH). The results revealed that the complex viscosity increased significantly with increasing urethane ionic group content due to the physical crosslinking effect resulted from aggregation of ionic groups. The most reported literature present that the crystallization rate of PBSi could be improved by incorporation of ionic groups when its contents ranged from 1% to 5%. However, the complex viscosity of PBSi is much higher than that of PBS and retard to synthesize PBSi with higher ionic groups content. Thus, few studies focused on the synthesis of PBSi with high ionic groups (higher than 5%) and exploring theirs structure-property relationships. Furthermore, most the synthesis of these PBSis are based on the polycondensation of 1,4-butanediol and succinic acid in the presence of sodium sulfonated salts [19,25,27,38], sodium hydrogen sulphite [39], diethanolamine hydrochloride [26]. Strikingly, the charge in the ionic groups for the polymers (ionomers) are known to vary the molecules structure and then render their unusual properties [40,41]. An illustrative example of this approach is when aromatic copolyesters incorporated with ionic groups, the ionomers exhibit many new performances [34–36]. Ge et al. and Wang et al. introduced a monofunctional phosphinate monomer (sodium salt of 2-hydroxyethyl 3-(phenylphosphinyl)propionate, SHPPP) as an end-capping agent to both linear and hyperbranched PET, and demonstrated that the increase in complex viscosity by the corporation of SHPPP ionic group could improve anti-dripping behaviors of PET significantly [42,43]. Zhang et al. [13] designed and synthesized a PET ionomer containing a novel bisfunctional phosphinate monomer named 10H-phenoxaphosphine-2,8-dicarboxylic acid,10-hydroxy-,2,8-dihydroxyethyl ester, 10-oxide (DHPPO-Na), the incorporating of aromatic groups-containing monomer guaranteed PETis to achieve high melt strength and flame retardance properties. All the researches demonstrate that the insertion of cationic group in polyesters is much particularly attractive than that of copolymerization and traditional blend method. Ionization can expand advantageously certain properties for PBS due to the increase in polarity and intermolecular force. Consequently, gas barrier property, thermal conductivity, hydrolytic degradation and mechanical properties will vary significantly with the increase of cationic group content.

Unfortunately, the synthesis of polyester cationic ionomers is in initial stage and they meet much difficulty for introducing aromatic cationic groups into the polyester chain by melt polycondensation [40]. In this paper, we focus on the design and synthesis of a new PBS ionomer containing a novel bisfunctional phosphinate monomer named kalium salt of 10H-phenoxaphosphine-2,8- dicarboxylic acid,10-hydroxy-,2,8-dihydroxyethyl ester,10-oxide (DHPPO-K). PBS ionomers containing 1%–7.5% aromatic cationic groups content were synthesized by condensation polymerization of succinic acid and 1,4-butanediol in the presence of DHPPO-K. The crystallization properties, rheological properties, dynamic mechanical properties, oxygen permeability, thermal conductivity and physical properties are completely investigated their structure-property relationships. After that, the assessment of their basic properties also proposed to describe the preliminary evaluation in biodegradable films application.

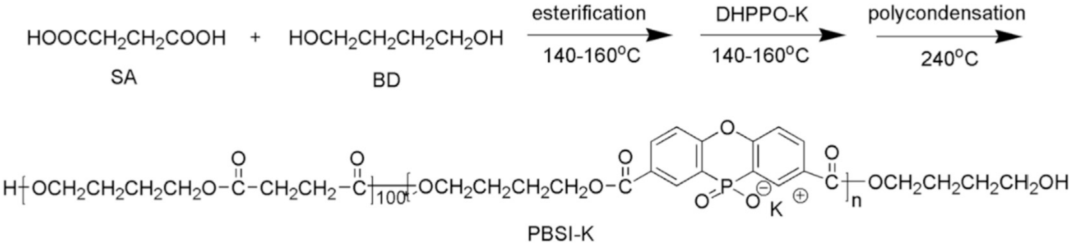
2. Experimental procedure

2.1. Materials

Succinic acid and 1,4-butanediol of AR grade were purchased from Macklin Biochemical Corp. (Shanghai, China) and used without further purification. Tetrabutyl titanate (Macklin Biochemical Corporation, Shanghai, China) with a concentration of 0.105 g/mL was prepared by dissolving in anhydrous toluene. The phosphorus-containing ionic monomer, kalium salt of 10H-phenoxaphosphine-2,8-dicarboxylic acid,10-hydroxy-2,8-dihydroxyethyl ester, 10-oxide (DHPPO-K), was prepared according to other reports [13,44–47]. All other reagents with AR grade were used without any further purification.

2.2. Synthesis of the phosphorus-containing PBS ionomer

PBS ionomer containing phosphorus ionic groups was synthesized by condensation polymerization of succinic acid, 1,4-butanediol and DHPPO-K. The preparation of PBSI3-K was shown as a representative (Scheme 1), where the number 3 represents the molar content (mol%) of DHPPO-K to succinic acid. Typically, SA (118 g, 1.0 mol), BD (108 mL, 1.2 mol), and tetrabutyl titanate (100 ppm, as catalyst) were



Scheme 1. Synthesis process of PBSIs-K, where s denotes the molar parts of DHPPO-K per hundred mole of BD (DHPPO-K: BD = s: 100 in mol), not the block length or repeating units.