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Structure effect of phosphite on the chain extension in PLA

Xin Meng [a], Guotao Shi [a], Weijie Chen [a], Chushi Wu [a], Zhong Xin [a, *], Ting Han [a], Yaoqi Shi [b]

[a] Shanghai Key Laboratory of Multiphase Materials Chemical Engineering and Production Engineering Department, School of Chemical Engineering, East China University of Science and Technology, Shanghai, PR China
[b] Shanghai Key Laboratory of Catalysis Technology for Polyolefin, Shanghai Research Institute of Chemical Industry, Shanghai, PR China

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ABSTRACT

PLA is synthesized from natural resource and can degrade easily, so it is a reasonable substituent of petroleum base plastic. Phosphites can increase the stability of PLA through the chain extension with PLA. In this paper, the molecular weights, complex viscosities and storage modulus of virgin PLA and PLA stabilized by different phosphites were characterized by gel permeation chromatography and rheometer. The results show that when there is a bigger substituent around the P–O bound in the phosphite molecule, the contact between the PLA and phosphite chain extender is inhibited and the chain extension becomes weak. In point of the three phosphite chain extenders of bis-2,2′-methyl-4,6-di-tert-butylphenyl phosphite (M46TBPP), tris(2,4-di-tert-butylphenyl) phosphite (Irgafos 168) and triphenylphosphite (TPP), the hindrance order around P–O bound is M46TBPP > Irgafos168 > TPP, and the hindrance of TPP is the smallest. So TPP takes the most effective chain extension in PLA. Furthermore, the by-product phenol formed due to chain extension of TPP has the weakest hydrogen donating ability, which makes PLA degrade weakest. So the average molecular weight values, complex viscosities and storage modulus of PLA stabilized by TPP are the biggest. In addition, the product, which was formed due to the chain extension of PLA and TPP, has some plasticization, so it makes PLA stabilized by TPP move free, crystallize easy. At last, compared to virgin PLA, PLA-TPP represents better mechanical properties.

1. Introduction

Polylactide (PLA), which is synthesized from natural resources, possesses high mechanical strength and can degrade into carbon dioxide and water in the end [1–3]. It is a satisfactory biodegradable plastic [2,3]. In point of most people, the sense of environment protection is becoming strong. An increasing number of people are interested in the preparation and application of PLA [4–6]. In recent years, there is an obvious progress in the purification and polymerization of lactic acid, so the price of PLA degreases continuously [6,7]. Now PLA are not only prepared into medical products with high added value, but also prepared into normal articles used in airplane, automobile and daily necessities. So the application of PLA is enlarged remarkable. It is reported that the amount of PLA will be the 47% of degradable plastics [8], and it will be the most reasonable substitute of petroleum plastics [9–12].

PLA can easily degrade to form low molecular weight fractions, which decreases the mechanical properties of PLA [13–15]. So maintaining and increasing the stability of PLA in the melt processing is very important. In the melt processing, chain extenders can increase the molecular weight of PLA through the reaction with the PLA, so the degradation can be inhibited efficiently [16–19]. Phosphite can reactive with the hydroxyl group and carboxyl group of polyester simultaneously, so it was used as chain extender of polyesters and polyesters-based composites [20–22]. Tris(nonylphenyl)phosphite (TNPP), which is one representative of phosphite, has been used to increase the stability of PLA in the melt processing. Najafi N et al. [23] studied the effect of TNPP on the melt stability of PLA/Clay composites, they found that the complex viscosity of PLA/Clay composite increased from 1050 Pa s to 2480 Pa s, when the 2 wt% TNPP was added into the composite. Furthermore, Ciceroa JA et al. [24] studied the effect of TNPP on the molecular decrease of PLA in the melt processing. They indicated that in point of virgin PLA, the molecular weight decreased 30% after processing, but the molecular weight maintained stable when TNPP was added. In a word, TNPP can increase the molecular weight of PLA through chain

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* Corresponding author.
E-mail address: xzh@ecust.edu.cn (Z. Xin).

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extension. But the application of TNPP is becoming limited, because nonyl-phenol formed due to the chain extension of TNPP is bad for the people's health. It is urgent to find other kinds of phosphite compounds. Although lots of phosphite compounds are being used in the stabilization of polypropylene widely, there are few reports on the application of other phosphite compounds exclude of TNPP in PLA. In this paper, several phosphite compounds were added into PLA, and the structure effect of those compounds on the chain extension in PLA were studied in order to help people to choose and design phosphite compounds in the future.

2. Experimental sections

2.1. Materials

PLA 2002D was purchased from Natureworks Company. Chain extenders triphenylphosphite (TPP) and tris(2,4-di-tert-butylphenyl) phosphite (Irgafos 168) were provided by Shanghai Chemicals Company and BASF Chemicals Company, respectively. Chain extender bis-2,2′-methyl-4,6-di-tert-butylphenyl phosphite (M46TBPP) was synthesized in our laboratory according to reference [25]. All structures of phosphites were shown in Table 1.

2,2- diphenyl-1-Picrylhydrazyl (DPPH) were provided by Sigma–Aldrich Chemicals Company. Phenol was produced by Shanghai Lingfeng Chemicals Company. 2,4-di-tert-butyl-phenol and bis-2,2′-methyl-di(4,6-di-tert-butyl)phenol were purchased from Nantong Fine Chemicals Company and were purified through re-crystallization before usage.

2.2. Sample preparation

2.2.1. Preparation of chain extended PLA

Before processing, the PLA were dried at 70 °C in a vacuum over for 12 h to avoid hydrolysis during processing. The processing of PLA in the presence of phosphite was carried out in a Haake-Buchler Torque Rheometer operating with a mixing chamber equipped with roller rotors. In the melt processing, the torque and temperature can be monitored as a function of time. Firstly, the PLA were plasticized in Haake-Buchler Torque Rheometer at 180 °C for about 10 min. Then several kinds of phosphites were added into the rheometer, respectively. After 15 min, the mixtures were taken out of the rheometer.

2.2.2. Preparation of chain extender used to test the hydrogen donating ability

In order to investigate the donating ability of compounds, the DPPH radical and phosphites were resolved in ethanol to prepare the solutions with the concentration of 2×10^{-4} mol/L, respectively. Then the radical solution was mixed with phosphite solution at the same volume as quickly as possible and the mixed solution was tested using ultraviolet spectrograph.

2.3. Sample characterization

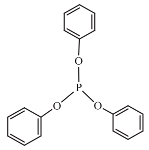
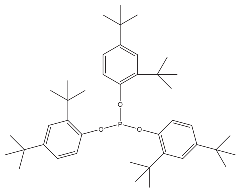
2.3.1. GPC testing

The average molecular weights of raw materials PLA, virgin PLA and PLA stabilized by different phosphites after processing were measured using Agilent GPC-50 gel permeation chromatography with differential detector. These experiments were performed at 35 °C in chromatography grade chloroform using PLgel5 Mixed-C columns at a flow rate of 1 ml/min. Conventional calibrations were performed using polystyrene standards.

2.3.2. Rheological analysis

Complex viscosities and modulus were measured in Physica MCR101 rheometer using standard 25 mm parallel plates. A special pressure canister containing molecular sieves was installed in the air inlet to the oven to exclude moisture and prevented hydrolytic degradation during testing. The tests were started when the temperature stabilized at 190 °C for about 5 min.The sample was loaded between the parallel plates and melted at 190 °C for 1 min. The parallel plates subsequently compressed the sample to 1.00 mm thick prior to each test. The strain and frequency range used during testing were 5% and 500–0.05 rad^{-1}.

Table 1
The formula of chain extenders.

Name	Structure
Triphenylphosphite(TPP)	
tris(2,4-di-tert-butylphenyl) phosphite (Irgafos 168)	
bis-2,2′-methyl-4,6-di-tert-butylphenyl phosphite (M46TBPP)