Thermochimica Acta 613 (2015) 113–120

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Thermal degradation and flame retardant mechanism of poly(vinyl chloride) plasticized with a novel chlorinated phosphate based on soybean oil

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ARTICLE INFO

Article history:
Received 27 April 2015
Received in revised form 13 May 2015
Accepted 15 May 2015
Available online 23 May 2015

Keywords:
Soybean oil
Phosphate ester
Poly(vinyl chloride)
Thermal properties
Flame retardant mechanism

ABSTRACT

A novel chlorinated phosphate based on soybean oil (CPSO) was synthesized and poly(vinyl chloride) (PVC) blends plasticized with CPSO were prepared. The flame retardant properties of PVC blends were investigated with LOI tests, SEM, TGA–FTIR and TGA–MS. The results indicated that LOI value of PVC blends plasticized with CPSO reached to 30.1%. The main pyrolysis gas products of PVC blends were H_2O, HCl, CO_2, CO and C_6H_6. Phosphorous-containing components generated during the thermal degradation of CPSO, most of which were retained in the char residue rather than that in the gaseous phase. They could promote formation of char residue. The char residue was blown by evolving gases which produced a foaming and expansion of the char layer. The carbonaceous char layer is effective in protecting the underlying material from further combustion.

1. Introduction

Poly(vinyl chloride) (PVC) is one of the most widely used engineering plastics [1]. It has broad application in many areas such as wire materials, window flames, wallpapers, pipes, flooring, cables, bottles, packaging and credit cards, audio records, medical tubing, blood bags and children toys [2]. However, as we know it is not easy to burn, but plasticized PVC is combustible and release smoke and poisonous gas while burning, because the plasticizers burn easily. The combustibility restricts the application of plasticized PVC materials. Thus, there is an urgent need to improve the flame retardancy of PVC products by using flame retardant plasticizer. Traditional intumescent flame retardant formulation is a blend of acid source, carbon source and gas sources. When the three parts are compounded appropriately, a synergistic flame retardant effect will be formed [3–4]. The flame retardancy of PVC products will be improved when they are plasticized with a plasticizer which could supply acid source, carbon source and gas sources in their thermal degradation. In addition, the raw materials of most of the materials are petroleum, scarcity of petroleum resources and the rising cost of petroleum products have led to the increasing trend toward developing of alternate sources of materials for industrial uses. Recently, there has been a growing interesting in the use of plasticizers obtained from renewable resources such as epoxidized safflower oil [5–6], epoxidized neem oil [7], epoxidized linseed oil [8], rice fatty acid [1], and epoxidized soybean oil [9–10]. Epoxidized soybean oil has been used as plasticizer of PVC for years, but the synthesis of soybean oil including flame retardant groups and the mechanism of flame retardant has never been reported. In this work, we prepared a novel bio-based plasticizer containing retardant groups based on soybean oil, and partly to replace the phthalate as secondary plasticizer for PVC.

In this study, a novel chlorinated phosphate ester based on soybean oil (CPSO) synthesized and characterized in laboratory. It was chosen to develop flame retardant PVC blends with enhanced flame retardancy. CPSO has excellent plasticizing effect, good thermal stability and charring effect. The aim of this study is to combine renewable resources of soybean oil and flame retardant group to improve the flame retardancy of PVC blends and keep the mechanical properties of PVC blends stable. A series of PVC-based flame retardant blends plasticized with CPSO were tested by LOI, scanning electron microscope (SEM) thermogravimetric analysis–Fourier transform infrared spectrometry (TG–FTIR), thermogravimetric analysis–mass spectrometry (TG–MS) and universal tensile testing machine. All of the investigations were carried out to further understand the mechanism of the flame retadancy of PVC blends plasticized with CPSO.

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http://dx.doi.org/10.1016/j.tca.2015.05.011
0040-6031/

2. Experimental

2.1. Materials

Soybean oil (SO) was provided by Arowana Group Ltd. (China) and was used without further purification. Phosphate, phosphorus oxychloride and glacial acetic acid were obtained from Nanjing Chemical Reagent Co., Ltd. Hydrogen peroxide, aluminum chloride and methylbenzene were supplied by Aladdin Chemical Co., Ltd. Polyvinyl chloride (PVC) was supplied by Hanwha (South Korea) with *K* value 65.0 and degree of polymerization 1300 ± 100.

2.2. Synthesis of epoxidized soybean oil (ESO)

100 g of soybean oil, 10 g of glacial acetic acid and 0.5 g of concentrated sulfuric acid was mixed in a four-necked round-bottom flask which was equipped with a mechanical stirrer, condenser pipe, thermometer and a constant pressure funnel. 60 ml of hydrogen peroxide solution was dropped in the reaction after 30 min and stirred at 60 °C for 8 h to finish epoxidation reaction. Then the reaction mixture was separated from water with separating funnel and washed 3 times with distilled water. Residual water was removed using a rotary evaporator at 60 °C. The chemical reaction process of ESO is shown in Fig. 1.

2.3. Synthesis of chlorinated phosphate based on soybean oil (CPSO)

15.3 g of phosphorus oxychloride and 0.15 g of aluminum chloride was mixed in a four-necked round-bottom flask which was equipped with a mechanical stirrer, gas collection device, thermometer and a constant pressure funnel. 100 g of ESO was dropped in the reaction in 3 h and stirred at 60 °C for 3 h to complete the reaction. Then the reaction mixture was separated from water using a separating funnel and washed 3 times with distilled water, residual water was removed using a rotary evaporator at 60 °C. The chemical reaction process of ESO was shown in Fig. 1.

2.5. Plasticization of PVC by CPSO

PVC was mixed with CPSO and DOP at different weight ratio using THF as the solvent. The mixture was thoroughly agitated by mechanical stirring for 1 h followed by sonication for 10 min. The samples were then cast into Petri dishes (diameter 19 cm) and dried at ambient temperature for 7 days to remove traces of residual solvent and to obtain thin films. The composition of PVC films is shown in Table 1.

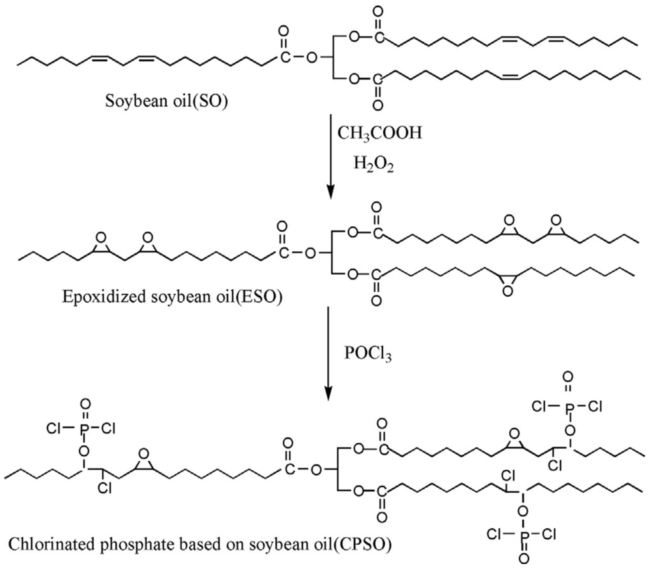

Fig. 1. The idealized reaction scheme for the synthesis of CPSO.

2.6. Measurements

FT-IR spectra of SO and CPSO were recorded on a Nicolet iS10 FT-IR (Nicolet Instrument Crop., USA) Fourier transformed infrared spectrophotometer. The spectra were acquired in the range of 4000–500 cm^{-1} at a resolution of 4 cm^{-1}.

^{1}H NMR spectra of SO and CPCO were recorded by using an AV-300 NMR spectrometer (Bruker, Germany) at a frequency of 400 MHz with tetramethylsilane as an internal standard.

The LOI values were obtained on a JF-3 oxygen index measuring instrument (Nanjing Lei instrument Co., Ltd., China) according to the standard of Plastics-Determination of burning behavior by oxygen index (GB/T 2406.1-2008, China).

The carbon layer of PVC films after LOI tests were investigated with a Hitachi 3400-1 (Hitachi, Japan) scanning electron microscope instrument, operated at 12 kV. The fracture of all surfaces was sputtered with gold to avoid electrostatic charging during examination.

The TGA–FTIR measurements were carried out using a 409PC thermal analyzer (Netzsch, Germany) coupled with a Nicolet iS10 FT-IR (Nicolet Instrument Crop., USA). About 10 mg of each sample was heated from 40 to 800 °C at a heating rate of 10 °C/min under N_2. The spectra were acquired in the range of 4000–500 cm^{-1} at a resolution of 4 cm^{-1}.

The TGA–MS measurements were carried out using a 409PC thermal analyzer (Netzsch, Germany) coupled with a QMS403C instrument (Netzsch, Germany). About 10 mg of each sample was heated from 40 to 800 °C at a heating rate of 10 °C/min under N_2 atmosphere. Mass scanning was carried out over the range m/v 2–200.

Tensile modulus, tensile strength, and elongation at break were determined according GB/T 1040.1-2006 (China) under ambient conditions, using E43.104 Universal Testing Machine (MTS Instrument Crop., China). The hardness was measured using an Age TH220 shore durometer (Guoanjie Instrument Crop., China). The reported values were the average of 6 samples.

3. Results and discussion

3.1. FT-IR

The structure of SO, ESO and CPSO were monitored using FT-IR. The spectra are depicted in Fig. 2. Several characteristic peaks were indicated in the spectrum of SO, the band at 3008.67 cm^{-1} is assigned to the absorption of =C—H bonds, the band at 2922.54 cm^{-1} and 2852.95 cm^{-1} is assigned to the absorption of methyl and methylene groups, respectively. The absorption of ester carbonyl group is at 1743.40 cm^{-1}, and the band at 1657.78 cm^{-1} is assigned to the absorption of —C=C— bonds. Comparing to the spectrum of ESO, the peaks of =C—H groups and —C=C— groups

Table 1
The composition of PVC blends.

Sample	PVC	DOP	CPSO
a	100	0	0
b	100	40	0
c	100	35	5
d	100	30	10
e	100	20	20