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A composition of phosphaphenanthrene groups-containing castor-oil-based phosphate plasticizer for PVC: Synthesis, characterization and property

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ABSTRACT

A composition of phosphaphenanthrene groups-containing castor-oil-based phosphate plasticizer (PGPP) was synthesized and characterized. Flame retardant PVC blends cooperated with different mass of PGPP were prepared. Flame retardancy of PVC blends were investigated with LOI, TGA, TGA-FTIR, TGA-MS and cone calorimeter. Flame retardant mechanism was also studied. The flame retardant performance of PGPP provides novel route for efficient use of vegetable oil and preparing advanced flame retardant PVC materials.

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Introduction

Poly(vinyl chloride) is an important thermoplastic plastic. Its excellent mechanical strength, thermal stability, flame retardancy and insulation characteristics have been paid more attention. It has been widely used in many PVC products such as in food packaging, children toys, medical devices, wire and cable and so on [1,2]. Flexible and durable PVC materials usually cooperated with a large amount of plasticizers. The traditional and common plasticizers are dioctyl phthalate (DOP) and dibutyl phthalate (DBP), which are easily diffused from PVC products to surrounding and cause the changes of property of PVC products. In addition, potential toxicity to human body has been paid more attention [3–9]. The flame retardant property of PVC materials will decrease when DOP cooperated with PVC due to the flammability of DOP, which will restrict the application of PVC materials from using in the field

with high requirement of flame retardant property such as wire and cable. But beyond that, raw materials for preparing DOP plasticizer are mainly derived from petroleum, scarcity of petroleum resources and the rising cost of petroleum products make the industrial way unsustainable. Recently, bio-based plasticizers such as cardanol-based plasticizer [10], epoxidized sunflower oil [11], epoxidized safflower oil [12], Low-Molecular-Weight glycerol esters [13], oleic acid polyester [14], rice fatty acid [1], and epoxidized soybean oil [15,16] has been synthesized and partly commercial application. But all of these plasticizers decreased the flame retardant properties of PVC materials, which restrict them from applying in harsh condition.

Flame retardancy of PVC materials can be enhanced by cooperating with antimony trioxide (Sb_2O_3), alumina trihydrate ($\text{Al}(\text{OH})_3$) [17], triphenyl phosphate and di-*n*-octylphenyl phosphate [18], but these flame retardant additives usually decrease mechanical property of PVC products, and they are mainly derived from petroleum. In order to prepare flame retardant plasticizer using bio-based raw materials, we prepared some flame retardant plasticizers using vegetable oil. The retardant mechanism of PVC materials cooperated with these plasticizers was also investigated.

Phosphorus-containing castor oil based plasticizer (PPC) was synthesized from castor oil, formic acid, phosphate, hydrogen peroxide (H_2O_2) and diethyl phosphate [19]. It can be used as

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secondary plasticizer to enhance the flame retardant property of PVC materials. Flame retardant performance of plasticizer can be improved by enhancing relative content of phosphorus [20,21]. Castor oil phosphate ester has been used as auxiliary plasticizer of PVC systems, which improved the flame retardant performance and thermal stability of PVC materials. The using of castor oil phosphate ester makes limiting oxygen index (LOI) value of PVC blends reach 27.8% [22]. DOPO is a novel kind of phosphorus-containing flame retardant, which has been paid more attention because of its high reactivity and flame retardancy. DOPO and its derivatives have been used efficient flame retardants for epoxy resin, which were reported in many publication [23–27], but there is no report to use them as plasticizer for PVC materials. In this study, our group synthesized a composition of phosphaphenanthrene groups-containing castor-oil-based phosphate plasticizer for PVC. Its chemical structure was characterized with FT-IR, ^1H NMR and ^{31}P NMR in detail. Thermal property, flame retardant performance, mechanical property of PVC blends plasticized with the synthesized flame retardant plasticizer derived from castor oil was investigated. It is hoped that novel flame retardant plasticizer can thus be obtained from castor oil. Furthermore, flame retardant PVC materials can be prepared and used in harsh conditions.

Experimental

Materials

Castor oil (CO), phosphate, glycerol, calcium hydroxide, dioctyl phthalate (DOP) and glacial acetic acid were obtained from Nanjing Chemical Reagent Co., Ltd. Hydrogen peroxide, DOPO, acetic anhydride 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 .

Synthesis of castor oil polyol (COP) and epoxidized castor oil polyol (ECOP)

COP and ECOP was synthesized in previous study [28].

Synthesis of phosphaphenanthrene groups containing castor oil polyol (PCOP)

A total of 120 g ECOP and 30 g DOPO were mixed in a three-necked round-bottom flask which was equipped with a mechanical stirrer, condenser pipe and thermometer. The mixture was

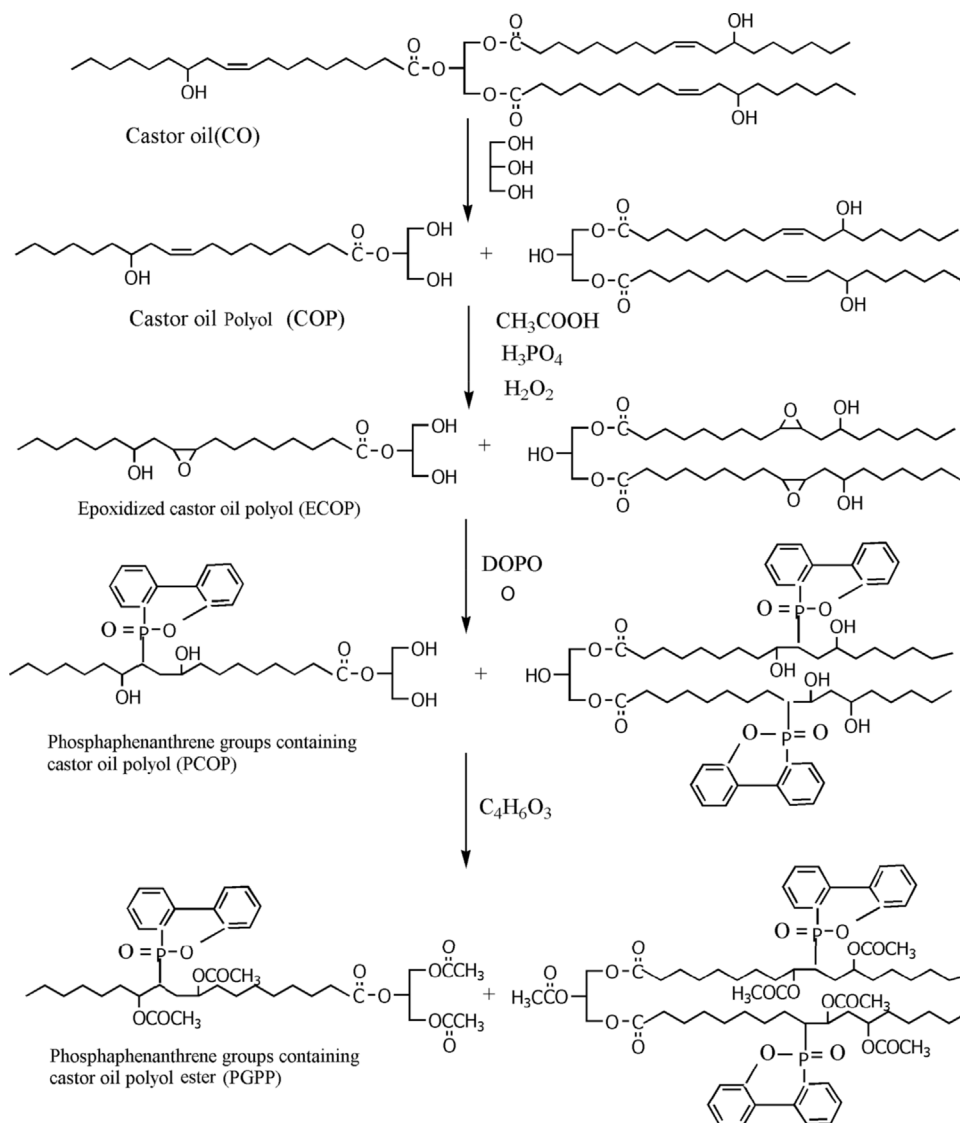


Fig. 1. The chemical reaction process of PGPP.

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