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Synthesis and application of a novel environmental plasticizer based on cardanol for poly(vinyl chloride)

Jie Chen[a], Xiaoying Li[a], Yigang Wang[a], Ke Li[a], Jinrui Huang[a], Jianchun Jiang[a,b,*], Xiaoan Nie[a,b,**]

[a] Institute of Chemical Industry of Forestry Products, Chinese Academy of Forestry, Nanjing, Jiangsu 210042, China
[b] Institute of New Technology of Forestry, Chinese Academy of Forestry, Beijing 100091, China

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ABSTRACT

A novel epoxidized cardanol phenyl phosphate ester plasticizer (ECPhP) based on cardanol was synthesized and characterized with ^{1}H NMR and ^{13}C NMR. Poly(vinyl chloride) (PVC) films plasticized with ECPhP as plasticizer were prepared. Thermal properties, mechanical properties and migration stability of PVC films were investigated with TGA, TGA–MS, DMA, dynamic thermal stability analysis, and tensile, volatility, extraction and exudation tests. Properties of the PVC films were explored and compared to those of petroleum-based plasticizer dioctyl terephthalate (DOTP). The results indicated that the epoxidized cardanol based phosphate ester had significantly higher thermal stability than DOTP, which could also improve thermal properties of PVC blends obviously. Furthermore, ECPhP could endow PVC resin with well-balanced properties of flexibility, strength and hardness. With the substitution of ECPhP into DOTP, migration resistance of PVC blends was enhanced which was mainly due to the increase of molecular weight. In addition, the thermal degradation processes of PVC films and possible interaction between plasticizers and PVC molecular were also discussed.

1. Introduction

A plasticizer was defined as "a substance or material incorporated in a material (usually a plastic or elastomer) to increase its flexibility, workability, or distensibility" by the council of International Union of Pure and Applied Chemistry (IUPAC) [1]. Industrially, plasticizers are an important class of low molecular weight nonvolatile compounds which are most widely applied in polymer processing as additives [2,3]. As the plastic industry continuously grows, the demand for plasticizers goes in the same direction [1]. It is well known that the most common plasticized polymer is PVC, and its processing consume over 80% of plasticizer production [4,5]. Furthermore, during the last decade, phthalates constitute more than 85% of the total plasticizer consumption of the PVC processing [5]. However, with the ever-increasing enhancement of environmental protection and health safety requirement, to limit the application range of phthalates is a tendency in the future [6–9]. Moreover, petroleum shortages and environmental concerns have encouraged extensive researches on chemical products based on renewable resources [10–14]. As a result, there is a growing interest in the use of bio-based plasticizers that are characterized by sustainability, availability and low cost. This group mainly includes epoxidized triglyceride oils from soybean oil [15], linseed oil [16], sunflower oil [17], fatty acid esters [18,19], glycerol esters [20], polyol ester [21] and polyester [22].

Cardanol is one of the renewable resources, which is an extracted product from cashew nut shell liquid [23,24]. Due in large part to its versatile chemical structure and low cost, cardanol had been commonly used to develop new eco-friendly functional materials [25–29] or additives [30–32]. Recently, cardanol derivatives had been used as plasticizer in the polymer and rubber industries and showed significant plasticizing effects [30,33,34]. In addition, cardanol derived plasticizers such as cardanol acetate [35,36], epoxidated cardanol acetate [35], cardanol derived glycidyl ether [37] and epoxied cardanol glycidyl ether [38] were prepared and revealed that they could be used as main or secondary plasticizers for PVC and replace phthalates. The present studies indicated cardanol derived plasticizers had good plasticizing effect, but they also showed some limitations in thermal and migration resistance. Due to the fact that PVC is sensitive to thermal degradation during

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[*] Correspondence to: Department of Bioresource Chemistry, Institute of Chemical Industry of Forestry Products, Chinese Academy of Forestry, Nanjing, Jiangsu 210042, China. Tel.: +86 25 85482488.

[**] Correspondence to: Department of Oil Chemistry, Institute of Chemical Industry of Forestry Products, Chinese Academy of Forestry, Nanjing, Jiangsu 210042, China. Tel.: +86 25 85482529; fax: +86 25 85482454.

E-mail addresses: bio-enegry@163.com (J. Jiang), niexiaoan@126.com, lumi1@126.com (X. Nie).

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processing and application, the migration of plasticizer caused changes in properties of the PVC products and possible toxic to humans [39], it is important to explore the renewable plasticizers with good thermal stability and migration resistance. Therefore, ahead of the versatility of the cardanol molecule structure, the authors look forward to research the chemical modification of this molecule by formation of epoxy and phosphate ester, and increasing the molecular weight of plasticizer.

In the present study, we aim to investigate the chemical modification of the cardanol molecule structure by formation of epoxy and phosphate ester, and increasing the molecular weight of plasticizer. A novel epoxidized cardanol phenyl phosphate (ECPhP) plasticizer was prepared. The plasticizing effect of this plasticizer used as secondary or main plasticizer on thermal properties, mechanical and migration resistance of PVC blends were investigated and compared to those of dioctyl terephthalate (DOTP). The thermal degradation processes and possible interaction between plasticizers and PVC molecular had also been proposed.

2. Experimental

2.1. Materials

Cardanol was procured from Shanghai Haohua Chemical Co., Ltd. (Shanghai, China) and was purified by distillation at 240–270 °C under 6–8 Torr. The product obtained was pale yellow in color, which contained 3.6% triene, 19.7% diene, 62.1% monoene, and 3.1% saturated compounds. Diphenyl chlorophosphate (99%), 3-chloroperbenzoic acid (75%) and DOTP (99.5%) were purchased from Aladdin Chemical Reagent Co., Ltd. (Shanghai, China). Dichloromethane and chloroform were obtained from Kelong Chemical Co., Ltd., (Chengdu, China). Sodium hydroxide (99 %), sodium bicarbonate (99.5 %) and sodium chloride (99 %) were obtained from Xilong Chemical Co., Ltd., (Shantou, China). PVC (S-1000) was purchased from the Sinopec Qilu Co., Ltd., (Zibo, China). Calcium stearate and zinc stearate were supplied by Changzhou Huaren Chemical Co., Ltd., (Changzhou, China).

2.2. Preparation of ECPhP

A three-necked round-bottomed flask equipped with a mechanical stirrer, reflux condenser and thermometer were charged with 50. 0 g of cardanol, 40 g of diethyl chlorophosphate and 6.0 g of sodium hydroxide. The mixture was dissolved in 150 ml chloroform and slowly heated to 60 °C and remained at that temperature for 3.0 h. Then the reaction mixture was filtered and the chloroform was recycled by vacuum distillation. The phenyl phosphate cardanol was obtained. Next, 32 g phenyl phosphate cardanol was added in a three-necked round bottom flask equipped with a mechanical stirrer, thermometer and reflux condenser. A mixture of 150 ml dichloromethane and 21 g 3-chloroperbenzoic acid was added slowly into the flask. The resultant solution was allowed to react at 30 °C for 3 h. After the reaction was complete, the reaction mixture was filtered and washed with a saturated solution of sodium sulfite, sodium bicarbonate, and sodium chloride solution, respectively. Finally, the organic phase was dried with anhydrous magnesium sulfate and then filtered. The filtrate was distilled under vacuum to recycle the dichloromethane and 28 g of a yellowish compound was obtained (yield: 82.6% relative to Cardanol). The ECPhP had an epoxy value of 3.3% and acid value of 1.6 mg/g. The synthesis routes of ECPhP are shown in Fig. 1.

2.3. Preparation of plasticized PVC specimens

A series of plasticized PVC specimens with different plasticizers were prepared. Firstly, PVC powder, plasticizers and thermal stabilizers (Ca soap/Zn soap = 3/1) were mixed using a mechanical mixer at room temperature for 5 min. Second, the mixture was compounded at 165 °C for 3 min by using double-roller blending rolls (Zhenggong Co., China). The PVC blends were obtained with a thickness of 2 mm. The composition of PVC blends is shown in Table 1.

Table 1
The composition of PVC blends.

Component (phr)	F0	F1	F2	F3	F4
Total plasticizer content	40.0	40.0	40.0	40.0	40.0
ECPhP content	0.0	4.0	8.0	12.0	40.0
DOTP content	40.0	36.0	32.0	28.0	0.0
Thermal stabilizers content	2.0	2.0	2.0	2.0	2.0

2.4. Characterizations

Fourier transform infrared (FTIR) analysis was conducted using a Nicolet IS10 spectrometer (Thermo Fisher Scientific Inc., USA) by an attenuated total reflectance method. The specimens were scanned from 4000 to 500 cm^{-1}.

^{1}H and ^{13}C NMR spectra of the compounds in deuterated chloroform ($CDCl_3$) were recorded on a Bruker ARX 300 spectrometer (Bruker Co., Germany) at room temperature.

Dynamic mechanical analysis (DMA) was measured by using a DMA Q800 (TA Instruments, New Castle, DE) in a dual cantilever mode with a frequency of 1 Hz. The testing temperature was swept from −60 to 80 °C at a heating rate of 3 °C/min. For each specimen, replicated tests were performed in order to ensure the reproducibility of data.

Thermogravimetric analysis (TGA) was carried out in a 409 PC thermogravimetric analyzer (Netzsch Co., Germany). Each specimen was scanned from ambient temperature to 600 °C under a nitrogen atmosphere at a heating rate of 10 °C/min.

The TGA–MS measurements were carried out using a 409 PC thermal analyzer (Netzsch Co., Germany) coupled with a QMS403C instrument (Netzsch Co., Germany). About 10 mg of each sample was heated from 40 to 600 °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.

Dynamic stability analysis was performed using a Haake Rheometer (Thermo Fisher Scientific Inc., USA) according to ASTM D 2538-02. The PVC/ plasticizer compounds were tested at 180 °C with a rotor speed of 30 rpm for 60 min. The dynamic thermal stabilizing time was defined as the time when the torque on the rotor starts to change abruptly [40].

Tensile properties were measured using a SANS CMT-4303 universal testing machine (Shenzhen Xinsansi Jiliang Instrument Co., China) according to ISO 527-2:1993. The cross-head speed was set at 10 mm/min. All specimens were conditioned at 23 °C for 1 day prior to tensile testing. Five specimens were prepared for each group to obtain an average value.

The Shore A durometer hardness was determined according to ASTM D224029. Five measures at 15 s per specimen were performed.

Volatility tests were determined by ISO 176:2005, the activated carbon method. The specimen was placed on the bottom of a metal container and about 120 cm^3 of activated carbon was spread over this specimen and then the lid was put on the container. The container was placed in the convection oven (Shanghai Suopu Instrument Co., China) at a temperature of 70 ± 1 °C. After 24 h, the container was removed from the oven and cooled at room temperature in a desiccator. The specimens were brushed and reweighed. The weight losses were measured before and after the heating. Three specimens were tested to obtain an average value.