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Tung oil based plasticizer and auxiliary stabilizer for poly(vinyl chloride)

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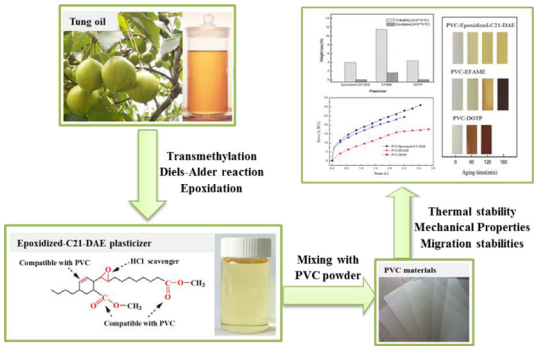
HIGHLIGHTS

- Tung oil was successfully converted into epoxidized dicarboxylic acid dimethyl ester (epoxidized-C21-DAE).
- Epoxidized-C21-DAE are introduced as primary plasticizer and auxiliary thermal stabilizer for poly(vinyl chloride)(PVC).
- The epoxidized-C21-DAE as a primary plasticizer for PVC significantly improved PVC thermal stability and flexibility.
- The epoxidized-C21-DAE plasticizer was compatible with PVC and could not be easily extracted

GRAPHICAL ABSTRACT



A tung oil derivative, epoxidized dicarboxylic acid dimethyl ester, was successfully prepared and used as both a green primary plasticizer and a high efficiency auxiliary thermal stabilizer for poly(vinyl chloride).

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ABSTRACT

A tung oil derived epoxidized dicarboxylic acid dimethyl ester (epoxidized-C21-DAE), was synthesized through transesterification, a Diels-Alder reaction, and epoxidation. The chemical structure of the epoxidized-C21-DAE was confirmed using Fourier transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance (^{1}H NMR) and carbon-13 nuclear magnetic resonance (^{13}C NMR). The thermal and migration stabilities and the mechanical properties of PVC samples were investigated using discoloration, tensile, exudation, volatility, and extraction tests as well as thermal gravity analysis (TGA), TGA–FTIR analysis, and dynamic mechanical analysis (DMA). The petroleum-based plasticizer, dioctyl terephthalate (DOTP), and the biobased plasticizer, epoxidized fatty acid methyl ester (EFAME), were chosen as controls and their properties compared with epoxidized-C21-DAE. The application of epoxidized C21-DAE as a biobased, primary plasticizer for poly(vinyl chloride) significantly improved PVC thermal stability over that of DOTP and EFAME. The mechanical properties of this type of PVC were superior to those of DOTP. In addition, the migration and volatility stabilities of epoxidized-C21-DAE were much better than EFAME. Epoxidized-C21-DAE could, therefore, be fully substituted for commercial DOTP or EFAME. Tung oil derived epoxidized-C21-DAE has good potential as a primary PVC plasticizer.

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1. Introduction

One of the most common polymers, PVC has a wide range of applications and is versatile and relatively inexpensive to manufacture [1]. However, the many polar chlorine atoms in pure PVC make it rigid at room temperature with a high glass transition temperature and low thermal stability. Thus, pure PVC is of little or no value. This problem is solved through the use of plasticizers and thermal stabilizers. Generally, plasticizers are added to polymeric materials to break up chain-chain interactions, leading to superior workability, better flexibility, and a lower T_g of the matrix polymer [2,3]. Plasticizers should possess polarizable portions (i.e., ester groups) to assure compatibility with PVC chains, and should contain more non-polar groups (i.e., alkyl chains) to accomplish the key task of plasticizing by breaking up chain-chain interactions and separating adjacent polymer chains [4,5].

Historically, plasticizers have high environmental costs. Dioctyl phthalate (DEHP or DOP) and dibutyl phthalate (DBP) account for >80% of the global plasticizer market [2,6,7]. Several phthalate esters (i.e., DEHP and DBP) are potentially toxic to human health and are ubiquitous contaminants in soil, water, air, and house dust [8–12]. Thus, there is a need for safer, greener, yet still profitable alternatives [13,14]. Dioctyl terephthalate (DOTP) is an excellent primary plasticizer for PVC. Although the performance of DOTP are similar to those of DOP (the ortho isomer), DOTP is less volatile, and is more resistant to lacquer marring. But most of all, DOP was more intractable than DOP during the process of biodegradation [15]. When DOP and DOTP were degraded by bacteria, the degradation rates of DOP and DOTP were 48 ± 4% and 73 ± 7%, respectively [15]. Many studies defined degradation as the destruction of the aromatic nature of the phthalic group in DEHP [16–19] and, only sometimes, as the subsequent mineralization of the breakdown products [20].

Due to these environmental concerns and petroleum shortages, biorenewable plant oils are a promising alternative for the production of synthetic chemical products [21–24]. Plant oil based plasticizers include epoxidized triglyceride oils from rubber seed oil [25], sunflower oil [26], soybean oil [26,27], linseed oil [28], and fatty acid esters [29]. Epoxy groups act as HCl scavengers during thermal degradation of PVC and bring excellent heat and light stability to PVC [30]. The epoxidized triglycerides or epoxidized fatty acid esters mentioned above are not only environment-friendly but also good candidates for PVC plasticizers and co-stabilizers [30].

Epoxidized soybean oil (ESO) has captured about 4.9% of the total plasticizer market [31]. However, epoxidized triglyceride oils (e.g., ESO and epoxidized sunflower oil) are commonly used as secondary plasticizers [27]. This is mainly due to the lower plasticizing efficiency of epoxidized triglyceride oils compared to DOP and DEHP and to the unreacted double bonds and hydroxide groups formed during the epoxidation [27,32,33]. These unreacted double bonds have relatively high molar mass (~926 g mol^{-1}), which reduces the compatibility of ESO and PVC. The plasticizing effect of epoxidized fatty acid esters is superior to that of ESO [27]. On the other hand, because the molecular volume of epoxidized fatty acid esters is small, its extraction, volatility, and migration stabilities are inferior to those of the phthalate ester plasticizers. This work, therefore, intends to synthesize a novel plant oil based plasticizer containing a functional epoxy group. Such a novel plasticizer would have excellent plasticizing and migration stability and could be used as a primary plasticizer to partially or entirely displace phthalate plasticizers.

In this work, a novel tung oil based epoxidized-C21-DAE was synthesized. This work demonstrates that this renewable, biobased plasticizer—with its alicyclic structure, dicarboxylic acid dimethyl ester structure, and epoxy group—offers excellent compatibility, thermal stability, plasticizing, and migration stability for PVC.

2. Materials and methods

2.1. Materials

The tung oil used in this study was purchased from the Luodian County Anling Vegetable Oil Plant, China. Methyl acrylate (CP, Shanghai Lingfeng Chemical Reagent Co., Ltd., China), methanol (≥99.5%, Nanjing Chemical Reagent Co., Ltd., China), KOH (≥85.0%, Xilong Chemical Company, China), NaCl (≥99.5%, Shanghai Jiuyi Chemical Reagent Co., Ltd., China), hydroquinol (≥98.0%, Chengdu Province Kelong Chemical Reagent Factory), formic acid (≥88.0%, Nanjing Chemical Reagent Co., Ltd.), phosphoric acid (≥85.0%, Chinasun Specialty Products Co., Ltd.), hydrogen peroxide solution(AR, 30 wt% in H_2O), $NaHCO_3$(≥99.5%, Sinopharm Chemical Reagent Co., Ltd., China), dioctyl terephthalate (DOTP, 97%, Aladdin Industrial Corporation), EFAME (Jiangsu Kat Petroleum New Energy Co., Ltd.) were used as received. Calcium and zinc stearates ($CaSt_2$ and $ZnSt_2$) were purchased from the Changzhou Jia Ren Wo Chemical Company. Polyvinyl chloride (PVC, S-1000) was supplied by the Shandong Qilu Co., Ltd., China.

2.2. Synthesis

Fig. 1 shows the synthetic route of the epoxidized C21-DAE plasticizer (epoxidized-C21-DAE). The eleostearic acid methyl ester (EAME), and C21dicarboxylic acid esters (C21-DAE) are also shown in Fig. 1.

2.2.1. Synthesis of methyl esters of tung oil fatty acids

Tung oil (1000 g), methanol (300 g), and KOH (7 g) were charged into a 1 L four-neck flask. The reaction lasted for 1.5 h at 70 °C. The mixture was separated using a separatory funnel, and the supernatant was then washed to neutral with saturated NaCl solution. After the supernatant was dried over Na_2SO_4 for 12 h, 830.0 g of a yellow product was obtained. Fig. 1 shows the gas chromatograph (GC) total ionization chromatogram and the compositions of methyl esters of tung oil fatty acids (METOFA). The obtained methyl esters consisted of 83.2% methyl eleostearate and were used for subsequent derivatization without further purification.

2.2.2. Synthesis of C21-DAE

METOFA (100 g) and hydroquinone (0.33 g) were added to a four-neck round bottom flask. When the temperature reached 100 °C, methyl acrylate (32.4 g) was slowly added. Once all of the methyl acrylate was added, the reaction continued for 5 h at 180 °C. The reaction mixture was distilled to collect the yellowish liquid distillate (95.8 g) between 150 °C and 260 °C, which contained 98.9% of the adduct methyl eleostearate and methyl acrylate (C21-DAE). The iodine value of the C21-DAE was 128.5 g/100 g (theory: 134.4 mg/g). The obtained C21-DAE was used for subsequent derivatization without further purification.

2.2.3. Synthesis of epoxidized-C21-DAE

A flask was charged with 0.6 g of phosphoric acid, 70.0 g of C21-DAE, and 9.7 g of formic acid. When the temperature reached 60 °C, 126 g of hydrogen peroxide solution was slowly added. Once all of the hydrogen peroxide solution was added, the reaction was continued for 5 h at 65 °C. The reaction mixture was dissolved in 50 mL of ethyl acetate and 40 mL of distilled water. The mixture was then separated from the distilled water using a separating funnel and was washed to pH = 7 with 2% $NaHCO_3$. The distilled water was then removed using a vacuum rotary evaporator to obtain a yellowish liquid. The acid value of the epoxidized-C21-DAE was 1.23 mg/g. The viscosity, iodine, and epoxy values of epoxidized-C21-DAE were 105 MPa·s, 33.7 g/100 g, and 0.23 mol/100 g, respectively.