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Epoxidized fatty acid tri-ester bio-plasticizer with anti-fogging performance comparable to diisodecyl phthalate

Siyu Pan¹, Demeng Liu¹, Xianchong Sun², Delong Hou¹, Jun Yan¹, Qi Zeng¹ and Yi Chen^{1*}

Abstract

The global scenario on PVC plasticizer is experiencing a drastic change from petroleum-based, toxic di-(2-ethylhexyl) phthalate (DEHP) toward renewable, non-toxic bio-alternatives. However, replacing diisodecyl phthalate (DIDP), a DEHP analogue specifically intended for plasticizing PVC automotive upholstery, with bio-alternative remains a challenge as few bio-plasticizer volatilizes from PVC as slowly as DIDP, a crucial aspect compulsorily required by automotive industry. Here, we demonstrate that covalently attaching two short esters at the α -position of all components of a traditional epoxidized fatty acid methyl ester *via* a two-step, hydrogen-to-ester nucleophilic substitution in a one-pot procedure yields an epoxidized fatty acid tri-ester bio-plasticizer with remarkably suppressed volatilization from PVC, and hence an extremely low fogging value comparable to DIDP. With this strategy in hand, DIDP, long deemed irreplaceable despite its toxicity and non-renewable nature, may ultimately be phased out.

Keywords Plasticizer, Epoxidized fatty acid methyl ester, Polyvinyl chloride, Anti-fogging, DIDP

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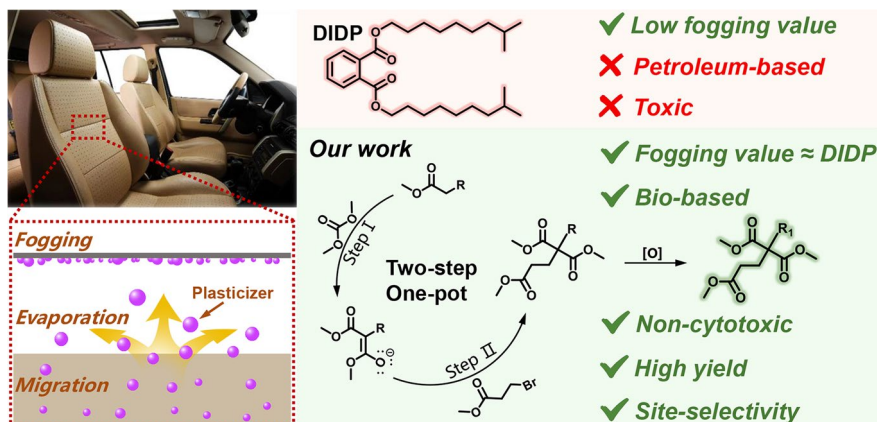
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Graphical Abstract



1 Introduction

Once polyvinyl chloride (PVC) is blended with an appropriate amount of plasticizer, the otherwise rigid polymer turns flexible, opening up a wide variety of applications from packaging to electrical wiring and medical supplies [1]. In 1930s, flexible PVC coating was first laminated onto one side of a fabric, yielding a cost-efficient assembly resembling genuine leather in appearance, which continues to benefit our daily life in multiple aspects [2]. Di-(2-ethylhexyl) phthalate (DEHP) was historically the most commonly used plasticizers for manufacturing PVC artificial leather. Despite its low-cost and good all-round performances, DEHP is petroleum-based, and thus non-renewable. In addition, increasing evidence suggests that DEHP is a reproductive toxicant capable of endocrine disruption [3, 4]. In this scenario, the last decade has witnessed an emergence of multiple bio-based alternatives, including epoxidized fatty acid methyl ester (EFAME), epoxidized soybean oil (ESO) and acetyl tributyl citrate (ATBC), as well as a surge of their application in PVC artificial leather industry.

Diisodecyl phthalate (DIDP) possesses the same core structure as DEHP, but has two longer, branched alkyl chains attached, each having 10 carbon atoms. Largely because of its higher molecular weight, DIDP volatilizes slowly from PVC even at high temperature, particularly suitable for producing PVC automotive upholstery artificial leather with anti-fogging performance. In automobile industry, fogging refers to volatilization of components from any upholstery material at high temperature that eventually condense at the cooler locations of the passenger compartment (e.g. windshield) to form a haze-like layer [5]. This thin layer of condensates reduces the visibility of driver, putting the safety of passengers at risk [6]. In the case of PVC artificial leather, plasticizers make up the vast majority

proportion of volatile substances; therefore, the automobile industry calls for plasticizers with extremely low volatility, or specifically, a low fogging value. Among all commercial bio-plasticizers, few can fulfil this requirement as well as DIDP. This fact has contributed to the consensus that DIDP, despite its non-renewable nature and reproductive toxicity [7], is irreplaceable by bio-based alternatives.

Here, we report a two-step/one-pot strategy that enables transformation of an ordinary EFAME normally displaying a fogging value > 20 mg to a volatilization-resistant bio-plasticizer. The feedstock we used was a naturally-occurring fatty acid methyl ester (FAME) containing $\sim 85\%$ methyl oleate and $\sim 15\%$ methyl stearate; the strategy reported herein allowed all components of the feedstock to be engineered with two extra short ester chains at the α -position. Governed by the interplay between two extra polar, PVC-compatible short esters and higher molecular weight relative to ordinary EFAME, the fogging value of the resulting epoxidized fatty acid tri-esters bio-plasticizer was found to reduce to a level comparable to DIDP.

2 Experimental

2.1 Materials

Fatty acid methyl ester (FAME) containing $\sim 85\%$ oleic acid methyl ester and $\sim 15\%$ stearic acid methyl ester, dimethyl carbonate (99.9%), sodium hydride (60%), methyl 3-bromopropionate (99%), formic acid (88%), soybean oil, and acetyl tributyl citrate (ATBC) were obtained from Macklin Biochemical Technology Co., Ltd. (Shanghai, China). Hydrogen peroxide (50%) was purchased from Chron Chemicals Co., Ltd. (Chengdu, China). Suspension PVC resin (SG-5, K-value 68–66) was kindly donated by Jinlu Resin Co., Ltd. (Chengdu, China). A thermal stabilizer mixture composed of calcium/zinc

stearate (calcium 6.6–7.4%, zinc 10.0–12.0%, Aladdin Biochemical Technology Co., Ltd., China) and 1-phenyl-icosane-1,3-dione (Juchuang Chemical Co., Ltd., China) in a weight ratio of 10:1 was prepared in-house.

2.2 Synthesis of epoxidized fatty acid tri-ester (EFATE) bio-plasticizer

Into a flask were added sodium hydride (8.8 g, 0.22 mol), dimethyl carbonate (180 g, 2.0 mol), and FAME (29.7 g, 0.1 mol), which was then heated up to 52 °C under a flowing N₂ atmosphere at 10 mL/min. After stirring for 28 h, the mixture was reduced to 50 °C, and methyl 3-bromopropionate (25.1 g, 0.15 mol) was added dropwise over a period of 1 h. Stirring was continued for another 8 h at the same temperature. After that, the reaction mixture was washed with dilute hydrochloric acid followed by ultrapure water. The organic fraction was subjected to distillation at 60 °C, affording fatty acid tri-ester (FATE, 96% yield).

FATE was then epoxidized to obtain EFATE bio-plasticizer, utilizing performic acid as an oxidant. First, FATE (100 g) and formic acid (3.9 g) were mixed at 50 °C, into which hydrogen peroxide (50 g) was added dropwise over a period of 2.5 h. Then, the oil-water mixture was intensely stirred at 50 °C for another 4.5 h. Finally, EFATE (99% yield) was obtained *via* quick removal of the residual formic acid aqueous solution under high vacuum. Using the same epoxidation procedure, epoxidized fatty acid methyl ester (EFAME, epoxy value = $4.2 \pm 0.04\%$) and epoxidized soybean oil (ESO, epoxy value = $6.3 \pm 0.05\%$) were also synthesized for comparison.

2.3 Preparation of plasticized PVC films

A powder mixture composed of PVC resin (30 g) and thermal stabilizer (0.6 g) was stirred at 90 °C for 6 min. Subsequently, the plasticizer (15 g), preheated to 90 °C, was added to the mixture, followed by continuous stirring for 10 min. The mixture was then plasticized by using HTK-200 cam rotors (Haer Machinery Co., Ltd., China) at 150 °C for 6 min, followed by continuous rolling using a CH-0201 two-roll mill (BP-8175-A, Dongguan Baopin Precision Instrument Co., Ltd., China) with a rotate speed of 10 rpm at 150 °C, yielding a transparent PVC film.

2.4 Characterization

Gas chromatography-mass spectrometer analyses were performed on an Agilent 7890 A/5975 C instrument equipped with an Rxi-5MS capillary column (30 m × 0.25 mm × 0.25 μm). ¹H nuclear magnetic resonance (¹H NMR) spectra were recorded on a Bruker AV II-400 MHz spectrometer with deuterated chloroform as deuterium reagent. Physicochemical parameters of the plasticizers,

including the Pt-Co color, density, acid value, iodine value, epoxy value and solidification point, were measured according to Chinese National GB Standards GB/T 605–2006 [8], GB/T 4472–2011 [9], GB/T 1668–2008 [10], GB/T 1676–2008 [11] and GB/T 1677–2008 [12], GB/T 510–2018 [13], respectively. A Horizon FTS fogging tester equipped with a VersaCool bath (Thermo Scientific, US) was used to evaluate the fogging values of the plasticized PVC films at 100 °C for 16 h according to the gravimetric method as specified in DIN 75,201: 2011 [14]. The evaporation loss of pure plasticizers was also tested on the fogging tester at 100 ± 0.5 °C for 3 h, in which 10 g plasticizer sample was used for each test. To evaluate the plasticizer migration loss, the plasticized PVC films were placed between two absorbent backing discs according to ISO 177: 2016 [15]. The sandwich was then pressed at 70 °C for 7 days by using a flat bottom block of 5 kg. Plasticizer migration was finally quantified by the changes in mass of the absorbent backing discs. The glass transition temperature of the plasticized PVC films was measured using DMA 850 from TA Instruments. The sample (10 mm × 5 mm × 0.5 mm) was swept from –85 to 100 °C with a frequency of 1 Hz at a heating rate of 3 °C/min. Stress-strain curves of the PVC films (50 mm × 10 mm × 0.5 mm) were obtained by using AI-7000-SU1 testing machine (Gotech Testing Machines Co., Ltd., China) at 100 mm/min cross-head speed. In vitro cytotoxicity of the plasticizers was evaluated according to ISO 10993-5 [16]. L929 cells were cultured in DMEM complete medium with 0.1 mg/mL plasticizer for 3 days. After that, cell viability was evaluated by using MTT assay. Statistical significance was defined as a *p*-value less than 0.05.

Forcite module from Materials Studio 8.0 (Accelrys Inc., San Diego, CA) was used for molecular dynamics (MD) simulation that estimated the self-diffusion coefficient of the plasticizers in PVC matrix. In brief, a series of binary cells, containing a certain number of plasticizers and four atactic PVC chains with 75 repeat units in a weight ratio of about 50:50, were first constructed. Before MD simulation, geometry of the cells was optimized with a fine convergence level using a smart algorithm. Interatomic interactions were characterized using COMPASS force field. Then, a stepwise procedure involving five annealing cycles was applied using NPT ($P = 1 \times 10^{-4}$ GPa) ensemble, by which the system was heated to 800 K and then cooled back to 300 K at intervals of 5 K. Andersen and Berendsen algorithms were employed to maintain constant temperature and pressure, respectively. After annealing, an extra dynamic was carried out at 450 K for 30 ns. Then, self-diffusion coefficients, D_{α} , of the plasticizers were calculated from the slope of the mean-square displacement (MSD) versus time plot according to the Einstein relation [17]. After that, the annealed cell was

subject to another NPT ($P=1 \times 10^{-4}$ GPa) dynamics at 300 K for 1 ns. Trajectories were saved every 2000 steps and the final 5000 ps configurations were adopted for analyzing the binding energy, ΔE , between the plasticizers and PVC, which is defined as follows:

$$\Delta E = \frac{-(E_{PVC/plasticizer} - E_{PVC} - E_{plasticizer})}{N_i}$$

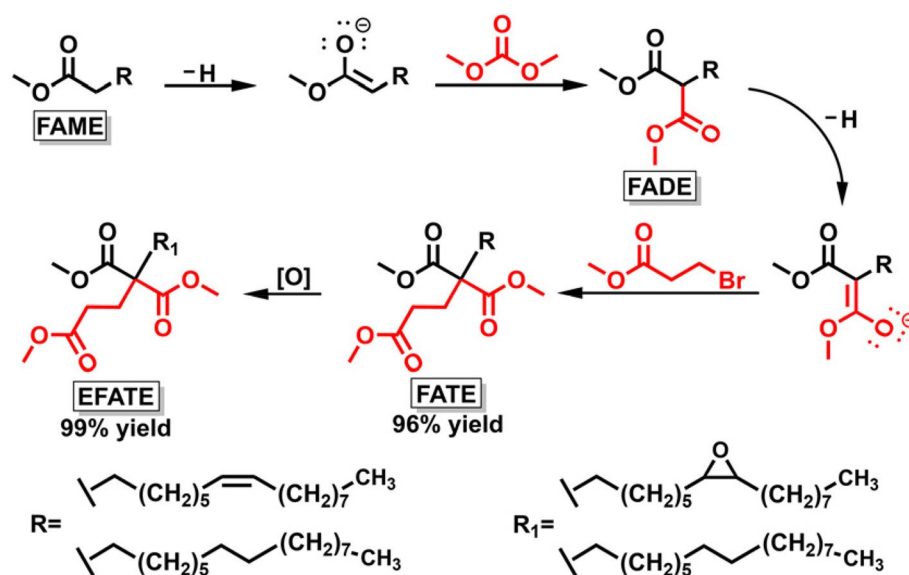
where, $E_{PVC/plasticizer}$ stands for the total energy of the PVC/plasticizer binary cells, E_{PVC} and $E_{plasticizer}$ represent the energies of PVC and plasticizer, respectively. N_i is the number of plasticizers of specie i .

3 Results and discussion

EFAME, derived from naturally occurring fatty acid methyl esters, is a bio-plasticizer gaining popularity due to its high plasticization efficiency, renewability, and degradability [18]. In general, commercial EFAME is a mixture mainly containing epoxidized fatty acid methyl esters, and a proportion of saturated fatty acid methyl esters, depending on the source of the feedstock [19]. In our previous research [20], we demonstrated that covalently attaching a second polar, short ester at the α -position of all components of ordinary EFAME *via* Claisen condensation with dimethyl carbonate significantly suppressed their volatilization from PVC matrix, leading to a significant reduction of its fogging value from >20 mg to a level (2.01 ± 0.08 mg) quite close to that of DEHP (1.32 ± 0.05 mg). With such progress in hand, we envisioned that attaching a third short ester to the resulting epoxidized fatty acid di-ester (EFADE) might push the fogging value limit of EFAME down to that of DIDP. Unfortunately, with only one

α -hydrogen left, EFADE could not react with dimethyl carbonate once again *via* the mechanism of Claisen condensation reaction. After initial struggles, we attempted to address this dilemma by using a two-step/one-pot strategy, as illustrated in Scheme 1. First, all components in the FAME feedstock were deprotonated to produce nucleophilic ester enolates, which then attacked the electrophilic carbonyl carbon of dimethyl carbonate, yielding fatty acid di-ester (FADE). The remaining α -hydrogen in FADE was subsequently deprotonated again to produce a highly stabilized β -diester enolate, followed by reacting with methyl 3-bromopropanoate in an S_N2 manner, yielding fatty acid tri-ester (FATE). Note that the above-mentioned cascade reactions occurred in a one-pot procedure, displaying inherent advantage of operational simplicity as it eliminated the step of intermediate purification to save resources and reduce waste. It was equally important that individual step occurred with high efficiency so that the overall percentage yield of FATE was as high as 96%. The as-prepared FATE was further epoxidized to yield our target product, epoxidized fatty acid tri-ester (EFATE, 99% yield).

The synthesis process of EFATE was monitored by using gas chromatography-mass spectrometry technique. Figure 1(a) and Table 1 revealed that the FAME feedstock we used was a mixture containing $\sim 85\%$ unsaturated oleic acid methyl ester (1) and $\sim 15\%$ saturated stearic acid methyl ester (2). After the two-step nucleophilic substitution, the gas chromatogram (Fig. 1(b)) showed total disappearance of the feedstock components, whereas two new components with retention times at 30.4 and 30.9 min were observed. These new components



Scheme 1 Synthesis procedure and chemical structure of EFATE

were identified as oleic acid tri-ester (3) and stearic acid tri-ester (4), given that their mass spectra showed strong fragment ions at m/z 218 and 145 (Fig. S1), corresponding to trimethyl propane-1,1,3-tricarboxylate and dimethyl 2-methylenemalonate cation, respectively. These results indicated all components of the feedstock had been engineered with two extra polar, short ester chains at the α -position. After epoxidation, a new peak (Fig. 1(c)) in the range of 34.3–34.8 min (5) attributed to epoxidized oleic acid tri-ester was detected, accompanied by a complete disappearance of unsaturated oleic acid tri-ester (3). The saturated component (4) remained unchanged given its resistance to epoxidation.

As shown in Fig. 2, EFATE exhibited distinct differences in its ^1H NMR spectra compared with the feedstock. Upon the two-step substitution, the integral of the OCH_3 signal (7) doubled in EFATE, relative to the integral of the CH_3 signal (1), whose chemical shift and

integral remained constant throughout the procedure. In addition, a strong OCH_3 signal (9) at 3.62 ppm and a CH_2 signal (8) at 2.23–2.26 ppm appeared, accompanied by a total depletion of the α -hydrogen signal (6), suggesting site-selectivity of the ester-attaching reaction. Note that the integral of the OCH_3 signal (9) was about half of that of the OCH_3 signal (7) in FATE, indicating almost stoichiometric substitution of the doubly α -hydrogen. FATE could be further epoxidized, as evidenced by a new oxirane signal (4) at 2.83 ppm in EFATE at the expense of the $\text{C}=\text{C}$ signal at 5.35 ppm.

Physicochemical parameters of the as-synthesized EFATE, including the Pt-Co color, density, acid value, iodine value and epoxy value, were measured, respectively, with the testing results showed in Table S1. These parameters were found to satisfy industrial requirement regarding commercial EFAME as specified in Chinese Industry standards HG/T 4390–2012.

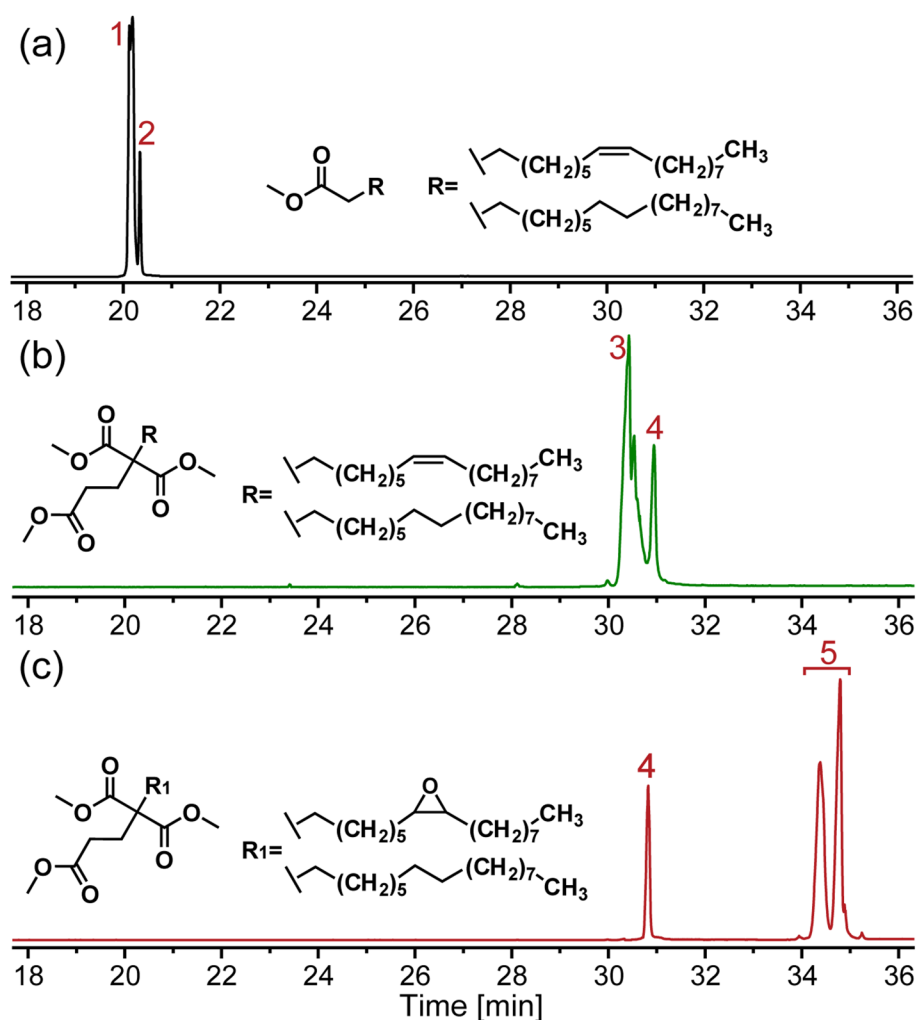


Fig. 1 Gas chromatograms of (a) FAME, (b) FATE and (c) EFATE. By comparing the mass spectra of each component in the chromatograms against NIST 08 database, the chemical structure of each component was deduced and illustrated in Table 1

Table 1 Composition of each component in Fig. 1

Peak	Retention time (min)	Composition	Molecular formula	Area (%)			Match scores
				FAME	FATE	EFATE	
1	20.3	Oleic acid methyl ester	C ₁₉ H ₃₆ O ₂	84.5			951
2	20.6	Stearic acid methyl ester	C ₁₉ H ₃₈ O ₂	14.4			962
3	30.4	Oleic acid tri-ester	C ₂₅ H ₄₄ O ₆		83.9		n/a ^a
4	30.9	Stearic acid tri-ester	C ₂₅ H ₄₆ O ₆		13.5	13.4	n/a ^a
5	34.3–34.8	Epoxidized oleic acid tri-ester	C ₂₅ H ₄₄ O ₇			82.7	n/a ^a
Others	n/a	n/a	n/a	1.1	2.6	3.9	n/a

^a NIST 08 database failed to identify this component. However, its chemical structure could still be deduced from the characteristic fragment ions at *m/z* 218 and 145 in the recorded mass spectra (Fig. S1) that pertained to trimethyl propane-1,1,3-tricarboxylate and dimethyl 2-methylenemalonate cation, respectively

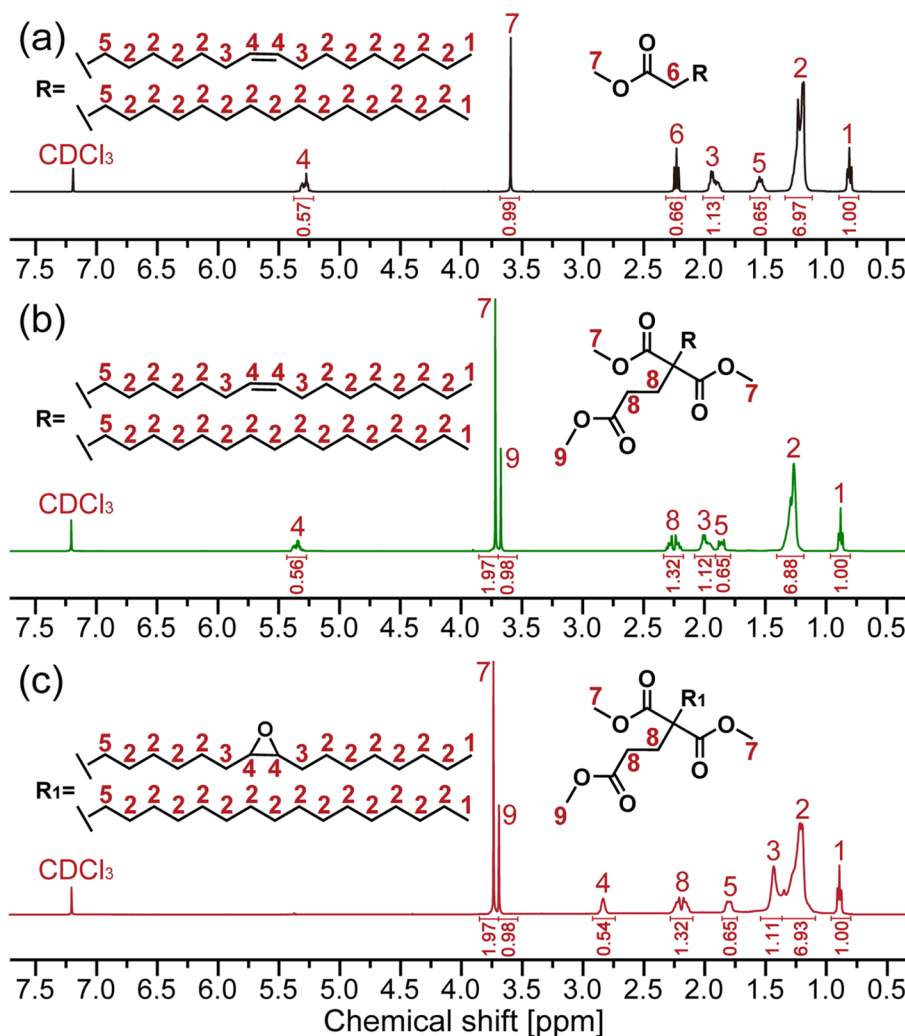


Fig. 2 ¹H NMR spectra of (a) FAME, (b) FATE and (c) EFATE. The signal corresponding to CH₃ protons (1) was selected as an internal standard as its chemical shift and integral remained constant throughout the two-step substitution procedure

To assess the anti-fogging performance of EFATE, we prepared a series of PVC films plasticized by EFAME, EFATE, and DIDP, respectively, followed by conducting a fogging test according to DIN 75201 [14]. As shown in Fig. 3, EFAME and ATBC showed a fogging value of 20.71 ± 0.15 mg and 11.43 ± 0.11 mg, respectively, significantly higher than that of DIDP (0.88 ± 0.09 mg). Thus, these two bio-plasticizers were unqualified to make PVC upholstery in automobile industry. As demonstrated in our previous research [20], after EFAME was engineered with one extra short ester at the α -position of all components *via* Claisen condensation with dimethyl carbonate, the resulting EFADE displayed improved resistance to volatilization, the fogging values of which decreased to 2.01 ± 0.08 mg, a level close to that of DEHP (1.32 ± 0.05 mg). In this study, we covalently attached two short esters at the α -position of all components in EFAME *via* a two-step, hydrogen-to-ester nucleophilic substitution in a one-pot procedure; the anti-fogging performance of the resulting EFATE improved dramatically, with its fogging value decreasing sharply to 0.90 ± 0.11 mg, comparable to that of DIDP (Fig. 3). Such improvement was inaccessible by inducing Claisen condensation between EFADE and dimethyl carbonate, as Claisen condensation only works for esters with two or three α -hydrogens [21]. Of note, ESO displayed a fogging value as low as 0.19 ± 0.06 mg in the fogging test (Fig. 3). However, industrial consensus has been reached that ESO is unsuitable for plasticizing PVC automobile upholstery given its significantly higher solidification point ($7 \sim 10$ °C), and hence compromised low-temperature resistance than DIDP whose solidification point is as low as -50 °C [22]. With two extra short ester chains at the α -position of all components, EFATE exhibited remarkably improved low-temperature

resistance, manifested by the observation that its solidification point decreased to $-40 \sim -45$ °C relative to ordinary EFAME ($5 \sim 7$ °C).

The fogging of a plasticizer is a two-step process including diffusion from the plasticized PVC bulk to the surface, followed by evaporation from the surface to the air/gas phase. To explore the mechanism underlying significantly improved anti-fogging performance of EFATE, the fogging value of pure EFATE bio-plasticizer was analyzed first on a fogging tester by heating at 100 °C for 3 h. The results showed that the evaporation loss of EFAME over the test reached 23.26 ± 0.18 mg, 83 times as high as that of EFATE (0.28 ± 0.05 mg) (Fig. 4(a)). Such improvement could be ascribed to the interplay of the following two aspects: (1) the average molecular weight of EFATE (454.5 g/mol) was higher than that of EFAME (310 g/mol) by approximately 47%, and thus the former has higher London dispersion forces to prevent evaporation; (2) the presence of two extra polar short esters in EFATE also endowed such bio-plasticizer stronger intramolecular dipole-dipole attractions that retarded evaporation.

To investigate how the ester group number in the plasticizer impacted its migration from the PVC interior to the surface, the plasticized PVC films were placed between two absorbent backing discs. Subsequently, the assembly was pressed at 70 °C for 7 days using a flat bottom block of 5 kg according to ISO 177 [15]. Plasticizer migration was finally quantified by the changes in mass of the absorbent backing discs. As shown in Fig. 4(b), the migration loss of EFATE ($1.1 \pm 0.11\%$) was only 16% of that of EFAME ($6.8 \pm 0.16\%$). Significantly suppressed migration might be attributed to the presence of the tri-ester group, which reinforced interaction with polar bonds in PVC through electrostatic and Van der Waals

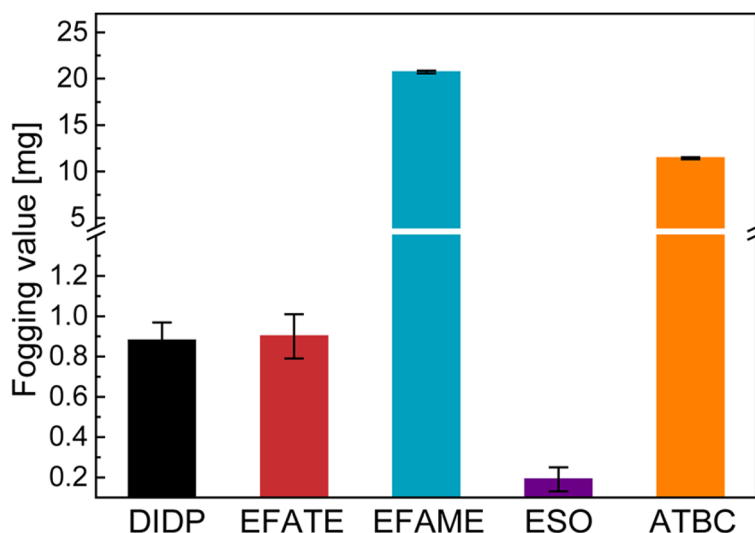


Fig. 3 Fogging value of PVC films plasticized by different plasticizers as measured according to DIN 75,201

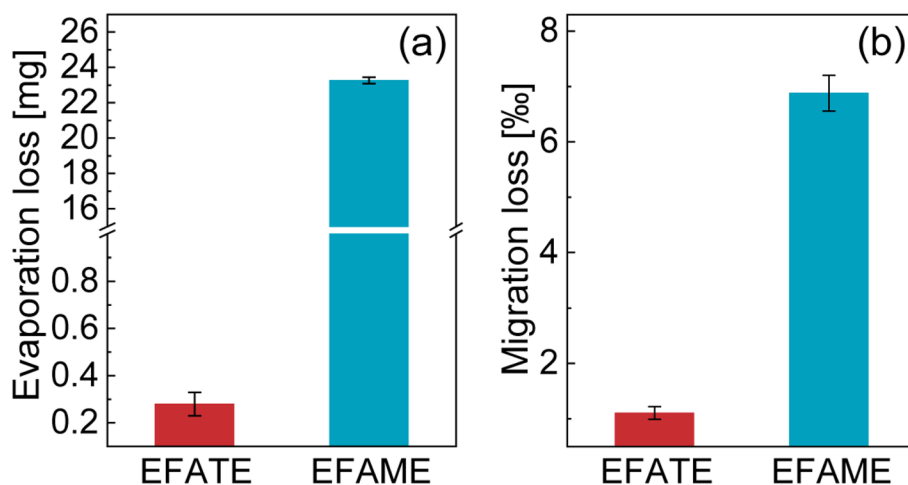


Fig. 4 a Evaporation loss of pure EFATE and EFAME at 100 °C for 3 h. b Migration loss of PVC films plasticized by EFATE and EFAME

forces. Suppressed migration of EFATME bio-plasticizer could also be demonstrated by ambient aging test (Fig. 5), in which the plasticized PVC films were hung in a glass container for 2 years. After that, a layer of plasticizers migrating to the sample surface was observed on EFAME-containing PVC film. In contrast, no plasticizer could be visualized on the PVC surfaces plasticized by EFATE or DIDP, suggesting they exhibited comparable migration resistance in long-term application. To confirm this experimental result, we constructed a series of fully atomistic PVC/plasticizer cells employing Materials Studio 8.0 simulation software. Each cell contained a certain number of plasticizers and PVC chains in a molecular weight ratio of about 50:50 (Table S2). After sufficient molecular dynamics equilibrium, the binding energy between one plasticizer molecule and the

PVC chains was analyzed. It was found that the calculated binding energy (42.6 ± 0.5 kcal/mol) of EFATE with PVC was higher than that of EFAME (34.0 ± 0.5 kcal/mol) by more than 25% (Fig. 6(a)), indicating reinforced interaction existed in the former. Accordingly, the calculated self-diffusion coefficient (Fig. 6(b)) of EFATE ($(9.2 \pm 2.8) \times 10^{-8}$ cm²/s) was found only 6.6% of that of EFAME ($(139.5 \pm 4.5) \times 10^{-8}$ cm²/s).

In addition, we also compared the plasticization properties of EFATE bio-plasticizer with DIDP and EFAME by measuring the glass transition temperature (T_g) and mechanical properties of the PVC films. Figure 7(a) illustrated the T_g of PVC films plasticized by DIDP, EFATE and EFAME, as measured by DMA technique. The results showed that the T_g of the PVC film plasticized by EFAME was 8.5 ± 1.3 °C. Although the T_g of the PVC

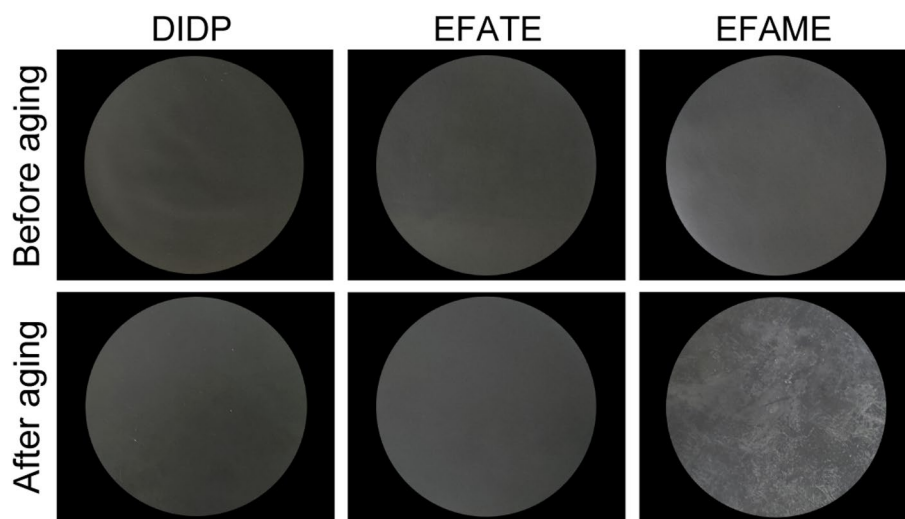


Fig. 5 Appearance of PVC films plasticized by DIDP, EFATE and EFAME before and after ambient aging for 2 years

film plasticized by EFAMTE increased to 24.6 ± 1.2 °C, it was still about 11 °C lower than that plasticized by the same amount of DIDP (35.2 ± 1.0 °C). As shown in Fig. 7(b), the elongation of the PVC film plasticized by EFATE ($208.3 \pm 6.9\%$) was higher than that plasticized by DIDP ($146.1 \pm 7.1\%$) by 30%, while the breaking strength of the former (14.8 ± 0.28 MPa) was quite close to latter (15.0 ± 0.23 MPa). These results indicated EFATE displayed higher plasticization efficiency than DIDP.

Finally, we evaluated the *in vitro* cytotoxicity of EFATE by MTT assay. As illustrated in Fig. S2, DIDP tended to kill L929 fibroblasts, but incubation with EFATE did not

cause a significant decrease in cell viability compared to the negative control, indicating our two-step/one-pot strategy had no detrimental effect on cytotoxicity of the resulting bio-plasticizer.

4 Conclusions

In summary, we described successful transformation of an ordinary EFAME normally unresistant to fogging into a structurally unique bio-plasticizer displaying an extremely low fogging value. Experimental studies and theoretical calculations revealed an important role of

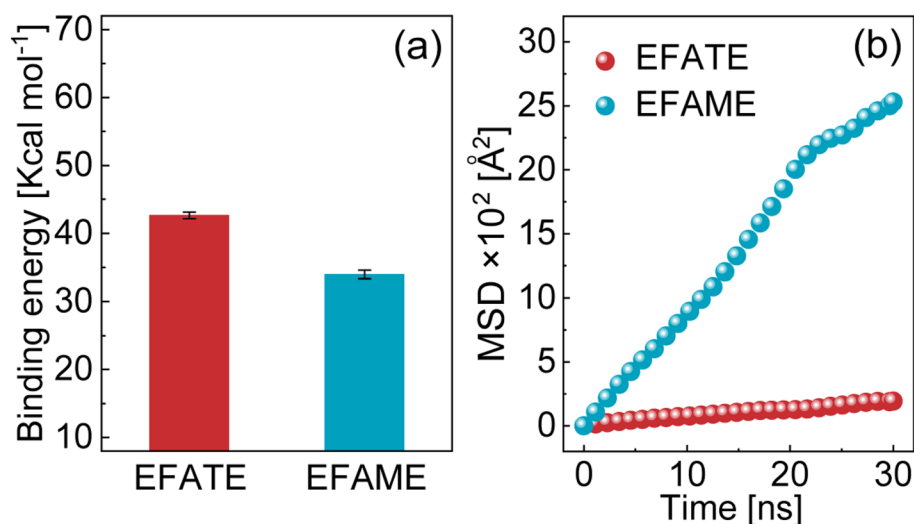


Fig. 6 **a** Calculated binding energy between PVC and each plasticizer molecule. **b** MSD versus time plots of the plasticizer within the PVC cell over a 30 ns NPT ($T=450$ K) dynamics run. Self-diffusion coefficient in the range of 2–12 ns was calculated by fitting the slope of the plots in (b) according to the Einstein relation [17]

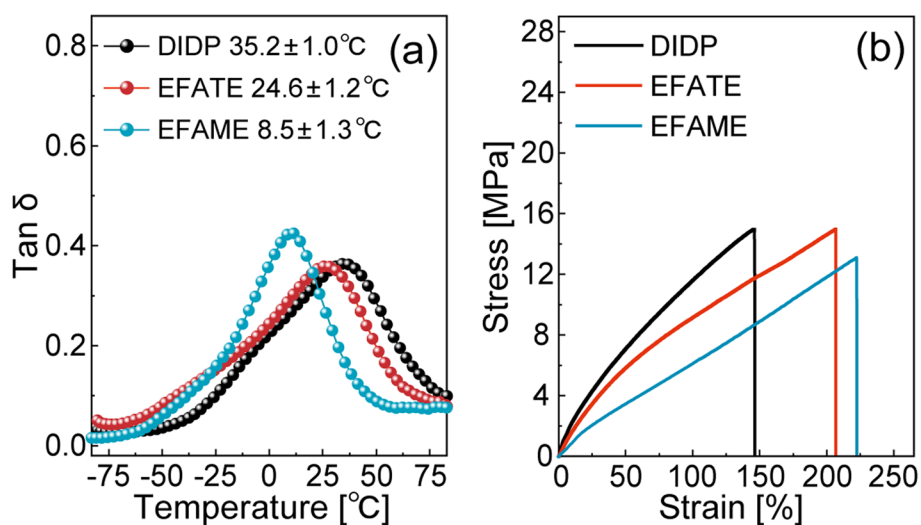


Fig. 7 Representative (a) DMA curves and (b) stress-strain curves of PVC films plasticized by DIDP, EFATE, and EFAME

the two extra ester chains introduced to all components of the feedstock by using our two-step/one-pot strategy, which suppressed both migration and evaporation of the resulting bio-plasticizer. This strategy was characterized by its high yield and site-selectivity.

Abbreviations

ATBC	Acetyl tributyl citrate
DEHP	Di-(2-ethylhexyl) phthalate
DIDP	Diisodecyl phthalate
EFAME	Epoxidized fatty acid methyl ester
EFAD	Epoxidized fatty acid di-ester
EFATE	Epoxidized fatty acid tri-ester
ESO	Epoxidized soybean oil
FAME	Fatty acid methyl ester
FADE	Fatty acid di-esters
FATE	Fatty acid tri-ester
PVC	Polyvinyl chloride

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s42825-024-00169-3>.

Supplementary Material 1.

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Authors' contributions

SP synthesized the plasticizer, interpreted the data, performed the cytotoxicity test and was a major contributor in writing the manuscript. DL tested the plasticization properties of the plasticizers and experimentally obtained the DMA and stress-strain curves. XS performed the NMR experiment. DH collected the mass spectrometry data. JY determined the physicochemical parameters and fogging value of the plasticizers. QZ performed the migration experiment and MD simulation. YC designed the technique route to synthesize the plasticizer and revised the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

All data generated or analysed during this study are included in this published article [and its supplementary information files].

Declarations

Competing interests

Yi Chen is a member of the editorial board of *Collagen and Leather*, and was not involved in the editorial review, or the decision to publish this article. All authors declare that there are no competing interests.

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