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Epoxidized dimeric acid methyl ester derived from rubber seed oil and its application as secondary plasticizer

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ABSTRACT: A novel plasticizer epoxidized dimeric acid methyl ester (EDAMe) based on rubber seed oil was synthesized. Chemical structure of EDAMe was characterized by Fourier transform infrared (FTIR) and gel permeation chromatography (GPC). Effects of EDAMe as secondary plasticizer and its substitution of commercial plasticizer dioctyl terephthalate (DOTP) in soft poly(vinyl chloride) (PVC) films were studied. The thermal properties, mechanical properties and migration stabilities of PVC films were explored with DMA, TG, TG–FTIR, dynamic thermal stability analysis, tensile and migration tests. The results indicated that the epoxidized rubber seed oil based ester has significantly higher thermal stability than DOTP. When DOTP was substituted with 20% (m/m) EDAMe, the results of initial decomposition temperature (T_i), 10% and 50% mass loss temperatures (T_{10} and T_{50}), and the first maximum weight-loss temperature rate (T_{P1}) reached 267.2 °C, 263.5 °C, 307.3 °C and 298.9 °C, respectively. Furthermore, flexibility of the obtained PVC films enhanced significantly with the adding of EDAMe. The migration stabilities of EDAMe was also investigated and showed good migration resistance. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43668.

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INTRODUCTION

Due to their potentially toxic and biological effects on human and environmental impact, the use of traditionally plasticizer for poly(vinyl chloride) (PVC), like dioctyl terephthalate (DOTP), is incontrovertibly becoming more limited.¹⁻⁴ In the past several decades, environmental concerns and petroleum shortages have triggered extensive research on chemical products based on renewsable resources.^{5–11} Currently, there is a trend to replace phthalates by plasticizers from renewable raw materials which are characterized by low toxicity, sustainability, ready availability and relatively low cost.^{8,12-16} Vegetable oils are the most widely used renewable raw materials for the chemical industries.^{17,18} The double bonds, hydroxyl and carboxy groups of vegetable oils are suitable to react with other chemical reagents.¹⁹⁻²⁴ But the excess use of these edible vegetable oil, such as soybean oil and canola oil, leads to food crisis, so present researchers are focusing on the non-edible oil sources for the renewable production.²⁵ Rubber seed oil is an unsaturated triglyceride abundantly available in rubber tree cultivations, which is mainly used as non-edible feedstock for biodiesel production.²⁶

Furthermore, due to its unsaturated double bonds, rubber seed oil and its derivatives usually have major applications in metal

soaps, epoxy compounds for the processing of polymers, alkyd resins and plasticizer.^{27–29}

Dimeric acid methyl ester (DAMe), produced by Diels-Alder reaction of conjugate and non-conjugated unsaturated fatty acid methyl ester (FAMe), is widely used in the fields of polyamides, polymer applications and as anticorrosives, etc.³⁰⁻³² Considering the DAMe could provide the alicyclic structure and flexible alkyl chains which is similar to phthalate, we look forward to expand its application in plastic industries. It has been suggested that the epoxy group, alicyclic structure and alkyl chain may be employed to endow plasticizer with good thermal stability and little toxic and biological effects.^{33,34} Currently, researchers have reported the synthesis and application of bio-based plasticizer, mainly include epoxidized triglyceride oils,^{35–37} fatty acid esters,³⁸ glycerol esters,³⁹ oleic acid polyester⁴⁰ and cardanol-based plasticizers.^{41–43} However, to the best of our knowledge, there is no published work on the synthesis of epoxidized dimeric acid methyl esters (EDAMe) and be used as plasticizer for PVC.

In the present study, we prepared and described the use of EDAMe based on rubber seed oil as a new type of secondary plasticizer for PVC. Its plasticizing effect on thermal properties, mechanical and migration resistance of PVC blends were

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characterized with DMA, TG, TG–FTIR, dynamic thermal stability, tensile, volatility, extraction and exudation tests and compared to those of DOTP. The aim of this work is to demonstrate that the novel epoxide plasticizer derived from renewable resources rubber seed oil can endow PVC blends with excellent mechanical property, thermal and migration resistance and offer new ideas for development of non-edible oil based plasticizer.

EXPERIMENTAL

Materials

Rubber seed oil was procured from Yunnan Huanqing Co., Ltd. (Yunnan, China). FAMe derived from rubber seed oil was obtained using the procedure in the literature 32 (methyl palmitate 10.28 wt %, methyl stearate 6.87 wt %, methyl oleate 28.18 wt %, methyl linoleate 37.48 wt %, methyl linolenate 17.08 wt %, with the content of unsaturated FAMe at 82.74 wt %). DOTP (99.5%) and anhydrous aluminium chloride (98%) were purchased from Aladdin Chemical Reagent Co., Ltd. (Shanghai, China). Ethyl acetate (99%), sodium bicarbonate (99.5%) and sodium chloride (99%) were obtained from Xilong Chemical Co., Ltd., (Shantou, China). Hydrogen peroxide (50 wt %) was purchased from Shanghai Akema Chemical Co., Ltd., (Shanghai, 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).

Preparation of EDAMe

15 g FAMe derived from rubber seed oil and 1g AlCl₃ catalyst were added and reacted at 240 °C for 6 h in a flask under dry nitrogen. After the reaction, the reaction mixture was cooled to 60 °C and then the upper layer was separated and distilled at 240 °C under reduced pressure over 20 min. The unreacted FAMEs were separated and the DAMe product was obtained. Then, in a typical experiment, 4.75 g DAMe, 0.15 g catalyst⁴⁴ and 10 ml ethyl acetate were added. After the mixture was heated to 50 °C, 2.1 g hydrogen peroxide was added. The reaction was allowed to continue at 65 °C for 1.0 h. After the reaction, the crude product was filtered and washed with a saturated solution of sodium bicarbonate and sodium chloride, and dried with anhydrous magnesium sulfate and then filtered. The crude product was purified using a silica gel column by ethyl acetate and n-hexane mixed solutions. Then the EDAMe product with an epoxy value of 3.22% and acid value of 1.64 mg/g was obtained.

Preparation of Plasticized PVC Test Specimens

The 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. Secondly, 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 I.

Characterizations

Fourier transform infrared (FTIR) analysis was conducted using a Nicolet IS10 spectrometer (Thermo Fisher Scientific Inc.,

Table I. The Composition of PVC Blends

| Component | FO | F1 | F2 | F3 |
|---------------------------|--------|--------|--------|--------|
| PVC (g) | 100.00 | 100.00 | 100.00 | 100.00 |
| EDAMe (g) | 0.00 | 4.00 | 8.00 | 12.00 |
| DOTP (g) | 40.00 | 36.00 | 32.00 | 28.00 |
| Thermal stabilizer (g) | 2.00 | 2.00 | 2.00 | 2.00 |

USA) by an attenuated total reflectance method. The specimens were scanned from 4000 to 500 cm^{-1} .

The gel permeation chromatographic analysis (GPC) were recorded on a GPC instrument with Styragel HR5E and HR2 (300 mm \times 7.8 mm, Waters Co., USA) columns as well as equipped with an Optilab-rEX refractive index detector (Wyatt Technology Co., USA). HPLC-grade tetrahydrofuran (THF) was used as eluent and the flow rate of the eluent was 1.0 mL/min.

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 60 °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 (TG) was carried out in a 409PC 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 TG-FTIR measurements were carried out using a 409PC thermal analyzer (Netzsch Co., Germany) coupled with a Nicolet iS10 FT-IR (Nicolet Instrument Co., USA). About 10 mg of each sample was heated from 40 to 600 °C at a heating rate of 10 °C/min under N₂. The spectra were acquired in the range of 4000–500 cm⁻¹ at a resolution of 4 cm⁻¹.

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 is defined as the time when the torque on the rotor starts to change abruptly.⁴⁵

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 seconds per specimen were performed.

Volatility tests were determined by ISO 176:2005, the activated carbon method. Place one specimen on the bottom of a metal container and spread about 120 cm³ of activated carbon over this specimen and then put the lid on the container. Place the container in the convection oven (Shanghai Suopu Instrument





Figure 1. FTIR spectra of DAMe and EDAMe.

Co., China) controlled at a temperature of $70 \,^{\circ}\text{C} \pm 1 \,^{\circ}\text{C}$. After 24 h, remove the container from the oven and allow it to cool 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.

Extraction tests were based on ASTMD 1239-98. The PVC specimens were immersed in distilled water, soybean oil and petroleum ether at 23 ± 1 °C and $50 \pm 5\%$ relative humidity. After 24 h, the extracted PVC specimens were rinsed with flowing water and then wiped up. Afterward, all of the specimens were dried in a convection oven (Shanghai Suopu Instrument Co., China) at 30 °C for 24 h and reweighed. The weight losses before and after the dipping were measured. Three specimens were tested to obtain an average value.

Exudation of the plasticizer was evaluated by placing a PVC specimen between two pieces of filter paper. These systems were then placed in a convection oven (Shanghai Suopu Instrument Co., China) at $60 \,^{\circ}$ C for 48 h. Then, the weight increment of



Figure 2. GPC chromatograms of DAMe and EDAMe.

Table II. GPC Results of DAMe and EDAMe

| Sample | M _n (g mol ⁻¹) | M _w (g mol ^{−1}) | Distribution index |
|--------|------------------------------------------|------------------------------------------|-----------------------|
| DAMe | 475 | 533 | 1.12 |
| EDAMe | 539 | 661 | 1.23 |

the filter papers was calculated. Three specimens were tested to obtain an average value.

RESULTS AND DISCUSSION

Characterization

The FIIR spectra of DAMe and EDAMe are depicted in Figure 1. In the spectrum of DAMe, there are several typical peaks: ==C-H stretching vibration absorption (3008 cm⁻¹), C-H stretching vibration absorption of methyl and methylene groups (2923 and 2850 cm⁻¹), C=O stretching vibration absorption of ester group (1738 cm⁻¹), vibration of hydrogen atoms adjacent to the unsaturated hexatomic ring (1583 cm⁻¹) and the asymmetric stretching of C=C (965 cm⁻¹).³² However, two obvious changes are observed in the spectrum of EDAMe. First, the inner unsaturated moiety at 3008 cm⁻¹ and 965 cm⁻¹ are absent because of the conversion to epoxide. Second, the characteristic features of the epoxy group are found at 884 and 842 cm⁻¹. These indicate that DAMe had been converted into EDAMe.

GPC technique was employed to analyze molar weights of the obtained DAMe and EDAMe. Figure 2 shows the elution chromatographs of GPC, and the corresponding values are given in Table II. It can be seen from Figure 2 that the area of elution time at 15-16 min. In the curve of DAMe, the strong peak at 16 min corresponded to the section of dimer main product. However, the weak peak around 15 min corresponded to the section of trimer or multimer by-products with high molar mass. Moreover, it is found that the elution time of EDAMe has decreased compared with that of DAMe by the epoxidation reaction. This fact is further evidenced by the change of molar



Figure 3. DMA in loss factors for the PVC films with different plasticizers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

| Sample | T _g (°C) | T _i (°C) | T ₁₀ (°C) | T ₅₀ (°C) | T _{p1} (°C) | T _{p2} (°C) | Residue (%) |
|--------|---------------------|---------------------|----------------------|----------------------|----------------------|----------------------|-------------|
| DOTP | _ | 222.00 | 199.89 | 257.91 | _ | _ | 1.12 |
| EDAMe | — | 354.20 | 258.36 | 395.82 | — | — | 2.51 |
| FO | 47.16 | 261.10 | 255.57 | 297.30 | 292.50 | 460.30 | 8.77 |
| F1 | 44.03 | 264.40 | 259.94 | 304.71 | 297.20 | 459.70 | 10.79 |
| F2 | 47.21 | 267.20 | 263.51 | 307.27 | 298.90 | 456.00 | 11.28 |
| F3 | 45.35 | 267.50 | 263.93 | 308.73 | 297.40 | 457.30 | 10.31 |

Table III. Glass Transition Temperature (T_e), Initial Decomposition Temperature (T_i), 10% and 50% Mass Loss Temperatures (T_{10} and T_{50}), Maximum Weight-Loss Temperature Rate (T_{P1} and T_{P2}) and Residue for PVC Films with Different Plasticizers

weights for the obtained DAMe and EDAMe (Table II). It is surveyed that both the weight and number-average molar weights $(M_w$ and $M_n)$ of EDAMe are larger than those of DAMe. All of these indicate the occurrence of the epoxidation reaction of DAMe. Moreover, it can be seen that the two compounds have small distribution indexs between 1.1 and 1.3, indicating a narrow distribution of their molecular weights.⁴⁶

Dynamic Mechanical Properties

Figure 3 compares the DMA spectra of PVC films with different plasticizers, the traces demonstrate a characteristic change in themal propertie assigned to a glass transition temperature (T_{q}) . All the PVC films displayed a single tan δ peak, indicating all the films are homogenous materials.47 Table III summarizes the T_{g} of different PVC blends. It can be seen that when DOTP was replaced with 10% (m/m) EDAMe (film F1), T_g dropped from 47.2 to 44.0 °C. However, continued increasing of the EDAMe concentration (film F2, F3) slightly increases the T_{e} . It can be explained that the molecular weight of EDAMe (about 539 g mol^{-1}) is higher than DOTP (about 390 g mol^{-1}), which would relatively reduce the content of the function groups and make T_g increased. Hence, EDAMe in small amounts could increase the plasticizing effect of compound plasticizers, and create a more efficient plastization system.¹⁴

Thermal Stability

TG technique was employed to analyze the weight loss behavior of PVC films. The TG curves of DOTP and EDAMe were presented in Figure 4. We observed the decomposition temperature and the mass loss temperature for different thermal degradation stage to trace the thermal degradation route. The results of initial decomposition temperature (T_i) , 10% and 50% mass loss temperatures (T_{10} and T_{50}) obtained using TG curves are given in Table III. For DOTP, the thermal degradation was observed at 222.0 °C, while the EDAMe showed an initial degradation at 354.2 °C Compared with DOTP, the EDAMe has increases of 58.5 °C and 137.9 °C in T_{10} and T_{50} respectively. Such large improvement in thermal stability might be due to the high stability epoxy group and higher molecular weight of EDAMe.⁴³ In addition, the char residues observed in the TG curves of DOTP and EDAMe were about 1.1% and 2.5%, respectively. Bade on the above, it can be concluded that plasticizer EDAMe has higher thermal stability.

TG instrument was also employed to analyze the weight loss behavior of PVC blends. Figures 5 and 6 show the TG and DTG curves of the PVC films plasticized with different plasticizers heated in nitrogen at the rate of 10 °C/min, respectively. The integrated obtained results for degradation processes were presented in Table III. It can be observed from the TG curves that the samples are mainly displayed two stages which in agreement with literature.48 The first stage degradation (about 230-380 °C) is the fastest and corresponded to dehydrochlorination of PVC and thermal decomposition of plasticizers.³⁰ The formation of aromatic compounds by the cyclization of conjugated polyene^{31,32} mainly occurred in the temperature range of 380-520 °C. DTG curves of PVC films exhibited two peaks at around 295°C and







Figure 5. TG curves of the PVC films.



Figure 6. DTG curves of the PVC films.

460 °C corresponding to the maximum weight-loss temperature rate (T_{P1} and T_{P2}). Furthermore, as shown in Table III, when DOTP was gradually substituted with EDAMe, the data for T_{i} , T_{10} , T_{50} and T_{P1} of PVC films increased gradually. But T_{P2} almost keep stable at around 459 °C, which is in agreement with the similar trend in the literature 49. When 20% DOTP was substituted by EDAMe (film F2), the T_{i} , T_{10} , T_{50} and T_{P1} reached 267.2 °C, 263.5 °C, 307.3 °C and 298.9 °C, respectively. These results indicated that EDAMe can improve the thermal stability of PVC films more than DOTP. In addition, the EDAMe can promote the formation of carbon residue, which can also enhance the thermal stability of PVC films.

TG-FTIR was performed to investigate the composition of the pyrolysis products of PVC blends containing different plasticizers. Figures 7 and 8 show the 3D TG–FTIR spectrum of gas phase in the decomposition of PVC film F0 and F2, respectively. The two peaks in Figures 7 and 8 occurred at 26.297 min and 42.090 min. According to the heating rate and initial temperature, the temperature at 26.297 min and 42.090 min were 300 $^{\circ}$ C and 460 $^{\circ}$ C, respectively, the temperature at peaks were consistent with the temperature at maximum rate of first and second degradation processes in TG. It can be seen from the



Figure 7. 3D TG-FTIR spectrum of gas phase of PVC film F0. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 8. 3D TG-FTIR spectrum of gas phase of PVC film F2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

spectra that the main gaseous products of the decomposition are H₂O (3593 cm⁻¹), C₆H₆ (3044 and 1508 cm⁻¹), HCl (2842 cm⁻¹), CO₂ (2358 cm⁻¹) and CO (2181 cm⁻¹). The maximum HCl concentration appeared at the first degradation processes. Compared with PVC film F0, the HCl concentration of PVC film F2 decreased as the EDAMe content increased. The concentration of H₂O, C₆H₆, CO₂ and CO of PVC films is similar to each other. The results are consistent with literature,^{49–51} which pointed out the epoxy groups could react to and absorb the HCl and delay the degradation events. Hence, the EDAMe is more effective on improving the thermal stability of PVC than the commercial plasticizers DOTP.

Tensile Properties and Hardness Character

Tensile properties of PVC film are important index to evaluate the plasticizing effect of plasticizer. The elongation at break, tensile strength and shore hardness of the PVC films are shown in Table IV. When DOTP was substituted with 10% and 20% (m/m) EDAMe (film F1 and F2), elongation at break could increase from 362.72% to 416.39%, and tensile strength could decrease from 26.36 MPa to 22.11 MPa. This result indicates that the addition of EDAMe significantly enhanced the flexibility properties of PVC matrix. On the other hand, when adding more EDAMe (up to 30%), the content of functional groups is relatively reduced due to the high molecular weight of EDAMe, thus leading to the elongation at break of film F3 decrease. Furthermore, as shown in Table IV, the shore hardness of the PVC blends containing EDAMe are similar to that of film F0, suggesting the similar hardness of all of the materials. The tensile and hardness results suggest that EDAMe

Table IV. Results Obtained from Tensile Measurements and Shore Hardness

| Sample | Elongation at break (%) | Tensile strength (MPa) | Shore hardness (HA) |
|--------|----------------------------|---------------------------|------------------------|
| FO | 362.72 ± 27.64 | 26.36 ± 2.84 | 89.1 ± 0.61 |
| F1 | 396.24 ± 10.46 | 22.11 ± 0.44 | 89.5 ± 1.03 |
| F2 | 416.39 ± 15.01 | 25.83 ± 0.59 | 89.3 ± 0.45 |
| F3 | 345.89 ± 16.95 | 22.87 ± 0.90 | 90.0 ± 0.97 |

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Figure 9. Effect of different plasticizers on dynamic thermal stability of PVC at 180 °C.

can endow the plasticized PVC film with good flexibility and hardness.

Dynamic Thermal Stability

Dynamic thermal stabilities of the PVC films with different plasticizers were tested by Haake torque rheometer at 180 °C and depicted in Figure 9. Table V summarizes the data of degradation time, balance torque and dynamic thermal stability time. Compared with the film F0, the dynamic thermal stability time of films containing EDAMe increased from 9.55 min to 15.10 min, as well as the degradation time delayed 8.92 min. Furthermore, the balance torques of films F1-F3 is similar to that of film F0. It can be perceived that EDAMe can improve the dynamic thermal stability and processability of PVC by extending the processing time and reducing the melt viscosity.⁴⁸ The results suggest that EDAMe increased the dynamic thermal stability time and the induction time of PVC, which agrees well with the TG results.

Migration Stability, Volatility Stability and Exudation Resistance

Migration stability, volatility stability and exudation resistance are important properties of plasticizer, which have been investigated by the extraction, volatility and exudation tests, respectively. The results are shown in Figure 10. PVC films showed

Table V. Results of Different Plasticizers on Dynamic Thermal Stability of PVC

| Formulation | Degradation time (min) | Balance torque (N m) | Dynamic thermal stability TIME (min) |
|-------------|------------------------------|----------------------------|-----------------------------------------------|
| FO | 11.74 | 4.10 | 9.55 |
| F1 | 16.31 | 3.92 | 13.59 |
| F2 | 17.54 | 3.79 | 15.03 |
| F3 | 20.66 | 4.33 | 15.10 |



Figure 10. Weight losses of PVC films after extraction, exudation and volatility testing.

different migration resistance when they were immersed in different solvents. When leached in organic solvents petroleum ether and soybean oil, all of the plasticizers shown poor migration resistance than in acidic and basic solvents. It can be obviously observed that the migration resistance in petroleum ether and soybean oil was improved with the substitution of EDAMe into DOTP. In addition, the migration stability of film F1-F3 in solvents 30% (w/v) acetic acid and 10% (w/w) sodium hydroxide were similar to that of DOTP. This is mainly because the migration stability is largely depended on the relatively high molecular weight and more branch chain of plasticizers.⁵² Films F1-F3 exhibited similar exudation resistance to film F0. This phenomenon indicates that all of the plasticizers shown good compatibility with PVC matrix.⁵³ As depicted in Figure 10, the volatility stability of plasticizers displayed a similar trend to the migration stability, which indicated that the volatility resistance of plasticizer could be improved significantly by adding EDAMe. So it can be concluded that the migration stability, volatility stability and exudation resistance of PVC films can be improved by incorporating EDAMe, which has the potential for medical devices, children toys and food packing⁵⁴ applications.

CONCLUSIONS

A novel plasticizer EDAMe was synthesized from rubber seed oil and incorporated into soft PVC films to evaluate its plasticizing effect, mechanical properties, thermal and migration stability. The EDAMe substitution of petroleum-based plasticizer DOTP was also explored. The DMA analysis indicated the EDAMe has higher plasticizing effect. The tensile tests showed that the EDAMe can endow PVC film with excellent flexibility. The results of TG and TG-FTIR suggested the thermal stability of PVC films increased with increasing the content of EDAMe. Furthermore, the migration stabilities analysis of plasticizers indicated that the EDAMe has good migration resistance. The present work provides a new approach for preparing non-edible oil based plasticizer. The EDAMe might be a potential secondary plasticizer for medical devices, children toys and food packing applications.



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