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Abstract: Waste cooking oil was modified to prepare bio-base plasticizers (a, b and c) with terephthalic acid, adipic acid and benzoic acid by transesterification, epoxidation and ring opening reactions, respectively. The polyvinyl chloride (PVC) films (a/PVC, b/PVC and c/PVC) were prepared using a, b and c as bio-base plasticizers. The epoxidation and ring opening reactions were mainly investigated through GC-MS analysis. The structures of bio-base plasticizers (a, b and c) were confirmed by Fourier transform infrared spectroscopy (FT-IR), 1H NMR and 13C NMR. The mechanical properties of a/PVC were as good as those of PVC films with the dioctyl phthalate (DOP) plasticizer. Meanwhile, the elongation at break of c/PVC reached 422%. The glass transition temperature ($T_g$) from dynamic mechanical analysis (DMA) was reduced to 30.6°C, 45.3°C, 23.6°C and 40.6°C, respectively when 40 phr of a, b, c and DOP plasticizer were added. Results of thermogravimetric analysis (TGA) illustrated that the thermal degradation stability of a/PVC films was better than those of c/PVC and DOP/PVC. The volatility losses of a, b and c were lower than that of the DOP. Bio-base plasticizers a and c exhibited excellent migration resistance in different solutions (distilled water, 50% ethanol (w/w)). The bio-base plasticizers b had a better plasticizing effect at low temperature.

Keywords: bio-base plasticizer; ring opening reaction; glass transition temperature; migration resistance; polyvinyl chloride (PVC)


1 Introduction

The increasing deterioration of the environment and depletion of petroleum resources force people pay more attention to the research and development of renewable resources (Bozell, 2010; Mekonnen et al., 2013). The production of materials needs to be changed from petro-based to bio-based; meanwhile, these processes should not compete with food production. Thus, using non-edible renewable resources to develop alternative bio-based materials has been a key point in the research (Azwar et al., 2013; Liu et al., 2016).

In 2014, the global consumption of edible oil was approximately 500 million t, 15% of which (approximately 75 million t) became waste cooking oil (Ma, 2016). Waste cooking oil is poor quality inedible oil which will cause serious environmental pollution if it is directly discharged as waste. The main chemical composition of waste cooking oil is the long chain fatty acid glyceride derived from vegetable oil or animal fats. Therefore, it can be used as the raw material for making various chemical products such as biodiesel, detergents, release agents for concrete, polyols, plasticizers, and most of them are fatty acid methyl ester derivatives. For example, epoxidized fatty acid methyl esters (EFAME) can be used as an auxiliary plasticizer for polyvinyl chloride (PVC) and is a high added-value product (Vyas et al., 2010; Lee et al., 2014; Noshadi, 2017).

It is estimated that 3.5 million t of phthalate plasticizers for the PVC which are completely coming from fossil oil are consumed per year (Storey et al., 1989; Bocqué et al., 2016). In addition, as persistent organic pollutants, the phthalate plasticizers pose potential threats to the environment and human health. Many countries have introduced strict bans regarding the use of phthalates in many specific applications, such as children’s toys, medical instruments, automobiles, food packaging, some materials used indoors (Benning et al., 2013; Dong et al., 2013; Kim et al., 2013; Jia et al., 2015; Bocqué et al., 2016). Therefore, the difficulty PVC plasticizers faced is that the phthalate plasticizers can not be replaced entirely by a nontoxic and environment-friendly plasticizer. Thus,
researchers have been developing alternative bio-based plasticizers with various degrees of success (Fenollar et al., 2009; Yin and Hakkarainen, 2011; Feng et al., 2015a). Bio-based plasticizers can be acquired from agricultural byproducts and wastes such as cardanol derivatives, starches, cellulose, citric acid, bio-based waste, agricultural byproducts and wastes such as cardanol (Bocqué et al., 2016). Therefore, it is significant to use some green approaches for efficient plasticizers (Feng, 2015b; Jia et al., 2018).

In this study, some types of bio-based plasticizers for the PVC were synthesized by modifying waste cooking oil with very user-friendly approaches. The synthesized plasticizers containing the ester groups and the benzene ring can interact with polymer chains thus bring compatibility; fatty chains can intersperse and intercalate between polymer chains, then increasing the intermolecular spacing and bringing mobility (Venturello and D’Aloisio, 1988; Sun et al., 2011; Wang et al., 2013; Ye et al., 2013). Some of them can completely substitute for the phthalate plasticizer (dioctyl phthalate, DOP), and the comprehensive performances of plasticized PVC films with the synthesized plasticizers were better than that with the DOP.

2 Experiment

2.1 Materials

Waste cooking oil (industrial grade, acid value is 10.4 mg KOH per gram, iodine value is 96 g per 100 g, and saponification value is 196 mg KOH per gram) was supplied by the Jiangsu Qianglin Bio-Energy & Bio-Materials Co., Ltd., Changzhou, China; DOP (99%, industrial grade) was supplied by the Bluesail Group Co., Ltd., Zibo, China. The PVC powder (KM-31, DP=1300±100, K value=71) was donated by the South Korea Hanwha Group, South Korea, all of which were reported by the supplier. Sulfuric acid (H2SO4, 98%), potassium hydroxide (KOH, AR), methanol (CH3OH, AR) and tetrabutylammonium chloride (TBAC, AR) were purchased from the Shanghai Aladdin Chemistry Co., Ltd., Shanghai, China, and used without further purification. Terephthalic acid (AR), benzoic acid (AR), adipic acid (AR), ethyl acetate (35% H2O2 (v/v)) and tetrahydrofuran (THF, AR) were purchased from the Nanjing Chemical Reagent Co., Ltd., Nanjing, China.

2.2 Synthesis of bio-based plasticizers for PVC

2.2.1 Fatty acid methyl ester (FAME)

One hundred gram (approximately 0.11 mol) of anhydrous waste oil and 18 g of KOH-CH3OH (0.028 g/g) solution were placed together in a 500 mL flask with a mechanical stirrer, condenser pipe and thermometer, and they were refluxed for 2 h. Then, the byproduct (crude glycerol) was removed from the lower layer by the standing and layering process after neutralizing by diluted acid to pH=7±0.5; the fatty acid methyl ester (FAME, 92 g, theoretical yield of the FAME was 104 g based on 100% triglycerides) was obtained by vacuum distillation of the upper solution at 250°C and 2.0 kPa. The acid value of the FAME was 0.2 mg/g, and the iodine value was 910 g/kg. The 1H NMR (CDCl3): δ: 5.39–5.54 (m, 4H), 3.63 (s, 3H), 2.35–2.21 (m, 2H), 2.03 (s, 4H), 1.67–1.50 (m, 2H), 1.31 (s, 2H), 1.29 (s, 18H), 0.84–0.89 (m, 3H).

2.2.2 Epoxy fatty acid methyl ester (EFAME)

As the epoxidation catalyst, 100 g of the FAME, 10 g of formic acid and 5 g of H2SO4 were mixed in a 500 mL flask, and 200 mL of H2O2 (35%, v/v) was dropped into the reaction over 60 min with stirring at 60°C. After 4 h of reaction, the mixture was separated from water with a separatory funnel and washed by distilled water to pH = 7±0.5. Then, the water was removed with a rotary evaporator at 60°C, and the residual moisture was removed by anhydrous sodium sulfate. The EFMAE was obtained (103.5 g) and analyzed by GC-MS (theoretical yield of the EFMAE is 105.7 g based on the iodine value, epoxy value is 4.2%, theoretical maximum epoxy value is 5.4%, and iodine value is 4.1 g/100 g, clear and colorless liquid). The 1H NMR (Fig. 3 (1), CDCl3): δ: 3.63 (s 3H), 3.10–2.82 (m, 4H), 2.35–2.21 (m, 2H), 2.03 (s, 4H), 1.67–1.50 (m, 2H), 1.31 (s, 2H), 1.29 (s, 18H), 0.84–0.89 (m, 3H).
2.2.3 General procedure for the ring-opening reactions of EFAME with organic carboxylic acids to give bio-base plasticizers (a, b and c)

In the first step, 100 g of the EFAME (approximately 0.26 mol of epoxy groups), 0.15–0.18 mol of carboxylic acids (—COOH) and 0.2 g of the TBAC as a catalyst were added into a three-necked flask equipped with magnetic stirring. The reaction was maintained under stirring at 100°C–180°C until the acid value was lower than 1.5 mg KOH per gram. The unreacted methyl ester (UFAME) was removed by 2.0 kPa decompressing distillation at 250°C, and the remained product participated in the next step. In the second step, the remained product and excessive acetic anhydride (2 mol) were placed in the three-necked flask, followed by stirring and refluxing for 3 h to finish the esterification. The excess acetic anhydride was removed by distillation. Then, the reaction mixture was washed by distilled water to pH = 7±0.5, and the product was dried by a rotary evaporator at 80°C. Finally, the bio-based plasticizers for the PVC were obtained. The major synthetic route is shown in Fig. 1.

2.2.4 Ring-opening of EFAME with terephthalic acid to give bio-based plasticizer a

A mixture of 100 g of the EFAME, 14 g of terephthalic acid (0.17 mol —COOH) and 2 g of the TBAC was heated at 170°C for 5 h, and the acid value of the mixture was 1.23 mg KOH/g. The work-up was carried out as described above. Yield of compound a: 66.2 g (theoretical yield of compound a, 73.9 g based on terephthalic acid), the UFAME of 49.4 g, appearance of yellow transparent

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**Fig. 1** Reaction route of bio-based plasticizers for PVC from modified waste oil
liquid, epoxy value=0.06%, viscosity=452 mPa·s at 20°C, acid value=0.32 mg KOH per gram. The 1H NMR (Fig. 3 (2), 500 MHz, CDCl₃) δ: 8.13 (s, 4H), 3.65 (s, 6H), 2.42–2.27 (m, 4H), 2.28 (s, 6H), 2.13–2.03 (m, 4H), 1.71–1.45 (m, 4H), 1.31 (s, 4H), 1.42–1.01 (m, 40H), 0.84–0.89 (m, 6H).

2.2.5 Ring-opening of EFAME with adipic acid to give bio-based plasticizer b
A mixture of 100 g of the EFAME, 11 g of adipic acid (0.15 mol —COOH) and 0.2 g of the TBAC was heated at 140°C for 5.5 h, and the acid value of the mixture was 1.46 mg KOH per gram. The work-up was carried out as described above. Yield of compound b: 58.3 g (theoretical yield of compound b, 64.5 g based on adipic acid), the yield of compound b, 64.5 g based on adipic acid, 0.04%, viscosity=345 mPa·s at 20°C, acid value=0.30 mg KOH per gram. The 1H NMR (Fig. 3 (3), 500 MHz, CDCl₃) δ: 8.10–7.91 (m, 2H), 7.56–7.26 (m, 3H), 7.42–7.09 (m, 4H), 5.05–4.78 (m, 4H), 3.65 (s, 6H), 2.42–2.23 (m, 4H), 2.08 (s, 6H), 2.13–2.03 (m, 4H), 1.71–1.55 (m, 8H), 1.52–1.43 (m, 8H), 1.42–1.01 (m, 40H), 0.84–0.89 (m, 6H).

2.2.6 Ring-opening of EFAME with benzoic acid to give bio-based plasticizer c
A mixture of 100 g of the EFAME, 22 g of benzoic acid (0.18 mol —COOH) and 0.2 g of the TBAC was heated at 90°C for 1 h, then it was heated up to 125°C for 4 h. The acid value of the mixture was 1.43 mg KOH per gram. The work-up was carried out as described above. Yield of compound c: 76.8 g (theoretical yield of compound c, 81.0 g based on benzoic acid), the UFAME of 44.8 g, appearance of yellow transparent liquid, epoxy value=0.07%, viscosity=354 mPa·s at 20°C, acid value=0.32 mg KOH per gram. The 1H NMR (Fig. 3 (4), 500 MHz, CDCl₃) δ: 8.13 (s, 4H), 3.65 (s, 6H), 2.42–2.27 (m, 4H), 2.08 (s, 6H), 2.13–2.03 (m, 4H), 1.71–1.55 (m, 8H), 1.52–1.43 (m, 8H), 1.42–1.01 (m, 40H), 0.84–0.89 (m, 6H).

2.3 Preparation of PVC films
The PVC resin powder (3 g) was mixed with 1.2 g of different plasticizers (40 phr, a, b, c and DOP), followed by adding 50 mL of the THF. The mixtures were thoroughly agitated at 40°C to form a transparent and homogeneous solution. The solutions were then cast into different glass petri dishes with a diameter of 22 cm, and then dried at ambient temperature for 7 d, followed by vacuum drying for 7 d at 50°C to remove the residual THF and obtain different plasticized PVC films (a/PVC, b/PVC, c/PVC and DOP/PVC) (Jia et al., 2015).

2.4 Characterization
2.4.1 Acid value, epoxy value, iodine value and viscosity
The acid value, epoxy value, iodine value and viscosity of the synthesized products were characterized according to the Chinese Industrial Standards of GB/T 1668-95, GB/T 1677-2008, GB/T 1676-2008, and GB/T 1660-2008, respectively.

2.4.2 Gas chromatography-mass spectrometry (GC-MS)
The Agilent 6890N/5973N GC-MS (Agilent Techn., Inc., HP-5MS) was used to analyze the composition of the EFAME and UFAME. The GC oven and injector temperature were designed to maintain at 280°C and 250°C, respectively, and the column temperature was controlled at 120°C for 1 min and then raised to 280°C for 20 min at 20°C/min. Helium (99.999%) was used as the carrier gas at the flow rate of 0.8 mL/min. The split ratio was preset at 50:1. Mass spectral data was obtained with an ion source temperature of 200°C, the detector voltage was 0.7 kV, and the scanning mass was set to range from 60 m/z to 540 m/z. Identification of the gaseous products was achieved by comparing the observed mass spectra to those in the National Institute of Standard and Technology (NIST) mass spectral library.

2.4.3 Fourier Transform Infrared Spectroscopy (FT-IR)
The FT-IR spectra were recorded on the Nicolet Magna-IR550 spectrometer (USA) with a resolution setting of 4 cm⁻¹ and a scanning range of 550–4000 cm⁻¹.

2.4.4 Nuclear magnetic resonance (NMR)
The 1H NMR and 13C NMR spectra of the products were obtained using the Bruker Avance AV II-400 NMR spectrometer (Germany), deuterochloroform (CDCl₃) and tetramethylsilane was used as the solvent and reference, respectively.

2.4.5 Mechanical properties
The mechanical properties of the PVC films (25 mm length (L) × 4 mm width (W) × 0.2 mm thickness (T)) were determined according to Chinese GB/T 1040.1-2006 with a crosshead speed of 100 mm/min under ambient conditions using the Universal Testing Machine (MTS Instrument Crop., China). The analysis of each sample was performed three times, and the average value was reported. The shore A/D durometer hardness was determined in accordance with ISO 868:2003. Three measurements at the speed of 15 s per sample (10 mm (L) × 10 mm (W) × 5 mm (T)) were performed.

2.4.6 Dynamic mechanical analysis (DMA)
The measurements were carried out on the dynamic mechanical thermal analyzer (Q800, TA Company, USA). Each specimen of the PVC films (80 mm (L) × 10 mm (W) × 0.2 mm (T)) was tested. A testing temperature was scanned from –80°C to 100°C with a heating rate of 3°C/min and a fixed frequency of 1 Hz.

2.4.7 Volatility tests
The volatility tests were conducted according to GB/T 1669-2001. The plasticizer (6–8 g, accurate to 0.0002 g)
was put into a weighed bottle with a cover and weighed, then the weighed bottle was placed in an oven controlled at (125±2)°C varying in time. Then, the weighed bottle was covered but not tightly and moved to the dryer; and then weighed when it had cooled to room temperature. Each specimen of the PVC film (60 mm (L) × 60 mm (W) × 0.2 mm (T)) was weighed and placed in an oven controlled at (170±1)°C. The specimens were taken from the oven and weighed again. The volatility loss was calculated according to Equation (1).

\[
\text{Weight loss} = \frac{W_1 - W_2}{W_1} \times 100\% \quad (1)
\]

where \(W_1\) is the initial weight of the test sample, and \(W_2\) is the final weight of the test sample.

2.4.8 Migration loss by leaching tests
The leaching tests were performed according to the ASTM D1239-98. The PVC films (60 mm (L) × 60 mm (W) × 0.2 mm (T)) were immersed into two solvents (distilled water and 95% (w/w) ethanol) at a temperature of (25±1)°C. Then the PVC films were rinsed and dried in an oven at 25°C for 24 h and reweighed. The migration loss was also calculated according to Equation (1).

### Table 1 Major compositions of EFAME and UFAME by GC-MS analysis

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Retention time (min)</th>
<th>Chemical structural formula</th>
<th>Area (%) EFAME</th>
<th>Area (%) UFAME</th>
<th>Matching degree (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.418</td>
<td>0.16</td>
<td>0.59</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>18.662</td>
<td>1.72</td>
<td>5.60</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>19.921</td>
<td>0.20</td>
<td>0.77</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>21.283</td>
<td>19.06</td>
<td>44.82</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>22.175</td>
<td>0.41</td>
<td>1.24</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>23.280</td>
<td>7.28</td>
<td>15.03</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>22.948</td>
<td>0.10</td>
<td>5.33</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>24.676</td>
<td>2.69</td>
<td>0.30</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>25.031</td>
<td>24.51</td>
<td>2.19</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>26.581</td>
<td>1.16</td>
<td>1.88</td>
<td>91</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>22.913</td>
<td>2.62</td>
<td>1.85</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>26.289</td>
<td>18.04</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>26.535</td>
<td>11.32</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

3 Results and Discussion

3.1 Synthesis and characterization
Figure 2 and Table 1 show the major compositions of the EFAME and UFAME by GC-MS analysis. Tiny amounts
unsaturated fatty acids (No. 7, 22.948 min) were found in the EFAME after epoxidation at the solvent-free and lower temperature conditions; a small amount of compounds containing a hydroxyl group (No. 9, 26.581 min; and No. B, 24.676 min) were detected, which were the by-products of epoxidation. Thus, the peroxophosphotungstate was proven to be an efficient epoxidation catalyst under greener conditions.

The unreacted products (UFAME) were obtained by vacuum distillation at 250 °C and 2.0 kPa, and the components of which were studied by GC-MS analysis, as shown in Fig. 2. The constituents of the EFAME and UFAME were the same, both of which contained compounds 1 to 10. However, the relative contents were quite different. The peak areas of the compounds that did not contain epoxy bonds significantly increased after the ring opening reaction, and the specific data are shown in Table 1. It was remarkable that both compounds 8 and 10 contains one and two hydroxyl groups, respectively, were by-products of epoxidation, while compound 8 readily reacted with carboxylic acid, and the main reason is that the hydroxyl group of compound 8 is a primary hydroxyl group with high activity. Additionally, the structure of the six-membered ring and double bond connecting with the β-C increased the nucleophilic character of the hydroxyl group. In addition, the peaks of B and C could not be recognized in the NIST mass spectral library (the matching was very low). However, both of them could be inferred to be C18 fatty acid methyl esters containing two or more epoxy groups according to the following three reasons. First, the quantities of B and C in the GC-MS analysis of the UFAME were very low; secondly, the peak times of compounds B and C were later than that of compound A; and lastly, according to previous studies, the raw material (waste oil) contained some linoleic acid (Fenollar et al., 2009).

Figure 3 demonstrates the 1H NMR and 13C NMR spectra of the EFAME and bio-based plasticizers (a, b and c). The 1H NMR and 13C NMR peaks of the epoxy group at δ: 2.8–3.2 and δ: 59.8–60.2 almost could not be found in the spectra of bio-based plasticizers (a, b and c). Small weak peaks at δ: 3.5–3.3 (1H NMR) and δ: 75.5–76.5 (13C NMR) represented the hydroxyl protons and carbon atoms, and the disappearing and weakening of peaks demonstrated that the ring opening and esterification reactions have been occurred. Due to the formation of the secondary ester groups from the esterification of acetic anhydride and hydroxyl groups, which was generated by the ring opening of the epoxy bond, and the peak at δ: 1.8–2.0 (1H NMR) and δ: 171.2–170.2 (13C NMR) were observed. After the ring opening reaction and esterification, the peak at 4.8–5.0 (1H NMR) and 72.1–74.6 (13C NMR) were discovered in a, b and c, representing the methyldiene proton linked to ester groups from the epoxy group. Figure 4 shows the FT-IR spectra of bio-based plasticizers a, b and c. After the ring opening reaction of the EFAME with different types of carboxylic acids, the absorption peak of the epoxy band at 840 cm⁻¹ disappeared, implying that the ring opening reaction of the epoxides occurred. Besides, there would be a strong and broad band of the hydroxyl peak at 3500 cm⁻¹ in the FT-IR spectra, while the hydroxyl peaks at 3500 cm⁻¹ of bio-based plasticizers a, b and c obviously decreased or disappeared because of the acetylation of hydroxyl groups. The absorption peak at 1580–1650 cm⁻¹ is typically the biggest evidence used to prove the existence of benzene rings (a and c).

3.2 Structure-property analysis of a–e as PVC plasticizers

The aims of the addition of plasticizers in plastic products are to increase the flexibility and elongation; reduce the elastic modulus, glass transition temperature (Tg) and brittleness temperature of the plasticized products; and make the plastic products have excellent processability.

3.2.1 Mechanical properties

The mechanical properties of the PVC films are a good effective way to evaluate the efficiency of plasticizers, as shown in Table 2. The mechanical properties of the a/PVC and c/PVC films are obviously better than that of b/PVC films, and are as good as that of the PVC films plasticized by the DOP. The elongation at break of c/PVC films reached 422% with a relatively low elasticity modulus and shore hardness. The main reason could be attributed to the chlorine atom in the PVC and the benzene ring in the molecular structure, which could increase the polarity of the molecules and reduce the physical crosslinking points between the chlorine atom, thus increased the compatibility with the molecules and the PVC resin. With the addition of plasticizers, the distance between the macromolecules of the polymer was increased, and the interaction between the polymer molecules decreased, which leaded to the low hardness of the PVC blend. The hardness of the PVC blend reflects the plasticizing efficiency of the plasticizer to some degree. The hardness of b/PVC was greater than that of the others, which indicated that bio-based plasticizer b for PVC was not as good as that of the others; the harnesses of a/PVC and c/PVC (containing a benzene ring plasticizer) showed little difference. Additionally, the results indicated that when compounds a and c were used as the plasticizers, they can endow PVC blends with well-balanced properties of flexibility, strength and hardness, as well as enhanced applicability of a flexible product.
Fig. 3  The $^1$H NMR and $^{13}$C NMR spectra of EFAME and bio-base plasticizers (a, b and c)
3.2.2 Dynamic mechanical analysis (DMA)

Figure 5 shows the DMA of the plasticized PVC films. All of the PVC films showed only a tan δ peak, indicating that the plasticizers were compatible with the PVC. The main peaks of tan δ plots were related to the $T_g$. Once the $T_g$ of the PVC blends is reached, there would be sufficient energy to overcome the attractive force between the chains, thus allowing for more chains moved within the blend, and then, the material would become macroscopically flexible. The $T_g$ value of the PVC composite without plasticizer is 76.5°C, which is shown in Fig. 5. The $T_g$ values of the PVC films with bio-base plasticizers a, b, c and DOP were 30.6°C, 45.3°C, 23.6°C and 40.6°C, respectively. In contrast, the plasticizing effects of compound b with the alkyl diacid modification was superior to those of the plasticizers a, c and DOP containing benzene ring at low temperature. This could be attribute to the plasticizers without a ring structure such as bio-based plasticizer b, which have better lubrication properties than the others at low temperature. However, the compatibility of bio-based plasticizer b with the PVC matrix is worse than that of the others. With the increase of temperature, the storage modulus of PVC/b is higher than that of the others. Therefore, in Fig. 5, the PVC/b curve started from a lower value of the storage modulus and crossed the others.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elongation at break (%)</th>
<th>Stress at break (MPa)</th>
<th>Elasticity modulus (MPa)</th>
<th>Tensile yield stress (MPa)</th>
<th>Shore hardness (HA/HD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure-PVC</td>
<td>25±10.2</td>
<td>54.3±1.7</td>
<td>2180.0±12.22</td>
<td>4.96±0.18</td>
<td>92.8±1.6 (HD)</td>
</tr>
<tr>
<td>a/PVC</td>
<td>405±21.7</td>
<td>43.2±2.31</td>
<td>12.5±0.67</td>
<td>3.29±0.18</td>
<td>94.2±2.6 (HA)</td>
</tr>
<tr>
<td>b/PVC</td>
<td>376±18.6</td>
<td>28.3±1.40</td>
<td>24.6±1.71</td>
<td>4.36±0.22</td>
<td>97.5±1.6 (HA)</td>
</tr>
<tr>
<td>c/PVC</td>
<td>422±25.6</td>
<td>34.7±2.10</td>
<td>10.7±0.83</td>
<td>3.13±0.19</td>
<td>93.7±1.8 (HA)</td>
</tr>
<tr>
<td>DOP/PVC</td>
<td>406±21.6</td>
<td>44.8±2.38</td>
<td>12.9±0.69</td>
<td>3.31±0.18</td>
<td>94.6±1.4 (HA)</td>
</tr>
</tbody>
</table>

3.2.3 Thermal degradation evaluated by TG analysis and temperature resistance

The thermogravimetric (TG) (a) and differential thermogravimetric (DTG) (b) curves of the PVC films (pure-PVC, a/PVC, b/PVC, c/PVC, and DOP/PVC) are presented in Fig. 6. All of the curves exhibited a three stage thermal degradation process. In the first stage of the PVC degradation, the most abundant volatile product was HCl at approximately 220°C–380°C. The second stage was at approximately 380°C–500°C, where the subsequent autocatalytic effect of HCl led to intensive dehydrochlorination. The thermal cracking of polyene chains resulting from the dehydrochlorination process contributed to the second weight loss. The third major weight loss was due to the oxidation of the char residue (Starnes, 2002; Feng et al., 2015a). Table 3 summarizes the
parameters of the TG and DTG, including the initial decomposition temperature \( (T_i) \); 10%, 20%–50% and 80% weight-loss temperatures \( (T_{10\%}, T_{20\%–50\%} \text{ and } T_{80\%}) \); temperature at the maximum weight-loss rate \( (T_{p1} \text{ and } T_{p2}) \); and the maximum weight-loss rates \( (R_1 \text{ and } R_2) \) in the first and the second stages of decomposition.

![Fig. 6](image)

**Fig. 6** The TG curves (a) and DTG curves (b) of pure PVC and plasticized PVC films

### Table 3  Thermogravimetric analysis data for pure PVC and PVC films with different plasticizers

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_i ) (℃)</th>
<th>( T_{5%} ) (℃)</th>
<th>( T_{10%} ) (℃)</th>
<th>( T_{20%–50%} ) (℃)</th>
<th>( T_{80%} ) (℃)</th>
<th>( R_1 (%/min)/T_{p1} ) (℃)</th>
<th>( R_2 (%/min)/T_{p2} ) (℃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure/PVC</td>
<td>202</td>
<td>267</td>
<td>278</td>
<td>286–314</td>
<td>461</td>
<td>18.1/302</td>
<td>4.06/468</td>
</tr>
<tr>
<td>DOP/PVC</td>
<td>194</td>
<td>239</td>
<td>259</td>
<td>276–302</td>
<td>432</td>
<td>16.27/302</td>
<td>2.78/462</td>
</tr>
<tr>
<td>a/PVC</td>
<td>202</td>
<td>257</td>
<td>263</td>
<td>284–322</td>
<td>448</td>
<td>10.4/294</td>
<td>3.27/464</td>
</tr>
<tr>
<td>b/PVC</td>
<td>183</td>
<td>232</td>
<td>263</td>
<td>278–303</td>
<td>460</td>
<td>14.1/289</td>
<td>3.31/466</td>
</tr>
<tr>
<td>c/PVC</td>
<td>196</td>
<td>251</td>
<td>269</td>
<td>282–322</td>
<td>459</td>
<td>12.0/288</td>
<td>3.81/462</td>
</tr>
</tbody>
</table>

With the addition of plasticizers, the DOP or the bio-base plasticizers a, b, c, the interactions between the PVC chains decreased and the thermal stability of plasticized PVC films was lower than that of the pure-PVC film without thermal stabilizer. However, the maximum weight-loss rate of pure-PVC was higher than that of the others. At the same time, the HCl from the PVC degradation could also promote the decomposition of the ester plasticizer. Due to the different thermal stabilities of plasticizers and the differences in compatibility with the PVC chain, some rules and differences could also be found in the decomposition of the PVC films with different plasticizers. The thermal degradation stability of the a/PVC films was better than that of the c/PVC and DOP/PVC films, which was attributed to the different thermal stabilities of the plasticizers. The thermal degradation stabilities of c/PVC and DOP/PVC films are better than those of b/PVC, which could be attributed to the differences in compatibility with the PVC chain.

#### 3.2.4 Migration loss evaluated by leaching tests

The weight losses of the PVC films by extraction in distilled water (a) and 50% ethanol (w/w, b) were shown in Fig. 7, respectively. The main factors related to migration loss are the molecular weight of the plasticizer and the compatibility of the plasticizer and PVC resin. The worse the compatibility is, the more the migration loss is; thus, no matter what kind of solvent, the migration losses of b/PVC films are larger than that of the others. The c/PVC films had relatively excellent stability in terms of the migration resistance. The larger the molecular weight was, the smaller the migration rate was, and the migration rates of a/PVC films were slower than that of the others in the initial stage. Additionally, based on the principle of dissolution in a similar material structure, the migration loss of plasticizers was larger in solvents of similar polarity. In distilled water, the extraction losses of a/PVC and c/PVC were very low. Compared with the DOP, bio-based plasticizers a and c had long aliphatic chains with high hydrophobicity, and consequently, the migration losses of a/PVC and c/PVC were lower than that of DOP/PVC in distilled water. By comprehensive comparison, bio-based plasticizers a and c were not inferior to the DOP. Therefore, the use of bio-based plasticizers a and c for the PVC could improve stability of the PVC films.

In addition, according to previous research, the compatibility between the plasticizer and PVC matrix was predicted based on the solubility parameters; the closer the solubility parameter of plasticizer to PVC’s, the better the compatibility between the plasticizer and PVC matrix.
The solubility parameter of the PVC and plasticizer can be determined using Equation (2), which is more accurate for plasticizers in low molecular weight (Small, 2007).

\[
\delta = \rho \frac{\sum F}{M} \tag{2}
\]

where \(\delta\) is the solubility parameter, and \(F\) is the molar attraction constant. \(\rho\) and \(M\) are the density and molecular weight of the plasticizer or chain unit of the polymer, respectively.

The value of different terms was calculated according to Equation (2) and their chemical composition and structure were reported in Table 4. It could be seen that the \(\delta\) of bio-based plasticizers \(a\) and \(c\) are slightly less than that of the DOP, indicating a good miscibility between bio-base plasticizers and PVC due to the high polar group (six ester groups or benzene) content. Besides, the molecular weight of bio-based plasticizers \(a\), \(b\) and \(c\) were higher. Consequently, the weight loss of extraction by organic solvent and water, as well as the volatilization of plasticized PVC were all relatively small.

### Table 4  Structures of components and solubility parameters for PVC and plasticizers

<table>
<thead>
<tr>
<th>Item</th>
<th>Molecular formula</th>
<th>Molecular weight (g/mol)</th>
<th>Density (20°C, g/m³)</th>
<th>Number of functional group</th>
<th>(\delta) (J/cm³)(^{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC(^*)</td>
<td>(\text{C}_2\text{H}_4\text{Cl}_2)</td>
<td>140 000</td>
<td></td>
<td>1300 1300</td>
<td>19.8</td>
</tr>
<tr>
<td>DOP</td>
<td>(\text{C}<em>{10}\text{H}</em>{12}\text{O}_4)</td>
<td>390</td>
<td>0.984</td>
<td>4 10 2 2 2 1 1 1</td>
<td>18.2</td>
</tr>
<tr>
<td>Bio-base plasticizers (a)</td>
<td>(\text{C}<em>{10}\text{H}</em>{12}\text{O}_{12})</td>
<td>875</td>
<td>0.991</td>
<td>6 28 4 6 1 1 1 1</td>
<td>17.8</td>
</tr>
<tr>
<td>Bio-base plasticizers (b)</td>
<td>(\text{C}<em>{10}\text{H}</em>{12}\text{O}_{12})</td>
<td>855</td>
<td>0.988</td>
<td>6 32 4 6 1 1 1 1</td>
<td>17.6</td>
</tr>
<tr>
<td>Bio-base plasticizers (c)</td>
<td>(\text{C}_{7}\text{H}<em>8\text{O}</em>{6})</td>
<td>476</td>
<td>0.989</td>
<td>3 14 2 3 1 1 1 1</td>
<td>17.9</td>
</tr>
</tbody>
</table>

Notes: *, average degree of polymerization (DP) of PVC is reported by the supplier; and the solubility parameter (\(\delta\)) of PVC and the molar attraction constant (\(F\)) can be found in the reference (Small, 2007).

#### 3.2.5 The FT-IR of PVC films

Figure 8 shows the FT-IR spectra of plasticized PVC and pure PVC. There are three peaks for the C—Cl stretching bands of pure PVC, representing at 688.62 cm\(^{-1}\) (TGTG sequence), 635.75 cm\(^{-1}\) (TTTT sequence) and 605.15 cm\(^{-1}\) (TT sequence) (Theodorou and Jasse, 1983; Zhang and Wang, 2000; Jia et al., 2017). After pure PVC was plasticized, the hydrogen bond between Cl—CH••••OC—(was formed, which led to the reduced energy of C—Cl, and thus, the absorption peaks of the C—Cl band shifted to lower frequencies and became wider. In comparison with the change of the absorption peak of the C—Cl band, the energies of the C—Cl bonds were reduced to different degrees with the addition of compounds \(a\) and \(c\) as plasticizers in the three PVC molecular chain sequences (TTTT, TGTG and TT). In the TGTG sequence of the plasticized PVC using bio-based plasticizer \(b\), the absorption peaks of the C—Cl bond were broadened. In the TTTT sequence, the absorption peaks did not move to lower frequencies. The TTTT sequence in the crystalline region of the PVC chain was attributed to the more stable sequence. However, bio-based plasticizer \(b\) did not affect the crystalline region of the PVC chain; thus, the plasticizing effects of bio-based plasticizer \(b\) were not as good as those of bio-based plasticizers \(a\) and \(c\).
Conclusions

Three bio-based plasticizers for poly(vinyl chloride) (a, b and c) were successfully synthesized using waste cooking oil as the raw material. The GC-MS analysis results showed that the tetrabutylammonium chloride (TBAC) were efficient for the epoxidation and ring opening of the epoxy catalyst under greener conditions. The structure-property analysis of bio-based plasticizers a, b and c for the PVC confirmed the following: first, the introduction of a benzene ring and ester bonds increased the polarity of the plasticizer molecules, which further improved the compatibility between the plasticizer and PVC resin; second, the higher molecular weight could reduced the volatility and extraction loss; third, the low temperature plasticizing effects of bio-based plasticizer b, which come from modified waste coking oil using alkyl diacid, were better than those of the others, and it could be used as the cold resistant auxiliary plasticizer for PVC. The bio-based plasticizers a and c derived from modified waste cooking oil using aromatic diacid could be used as temperature-resistant main plasticizers for the PVC to completely replace the DOP.

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