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Chemical routes to materials

Synthesis and application of a novel environmental C26 diglycidyl ester plasticizer based on castor oil for poly(vinyl chloride)

Jie Chen[1,2,3,*], Zengshe Liu[4], Xiaoan Nie[1,2,3,*], and Jianchun Jiang[4]

[1] *Institute of Chemical Industry of Forestry Products, Chinese Academy of Forestry, Nanjing 210042, Jiangsu, People's Republic of China*
[2] *National Engineering Laboratory for Biomass Chemical Utilization, Nanjing 210042, Jiangsu, People's Republic of China*
[3] *Key Laboratory of Biomass Energy and Material, Nanjing 210042, Jiangsu, People's Republic of China*
[4] *USDA, ARS, National Center for Agricultural Utilization Research, Bio-Oils Research Unit, 1815 N University St, Peoria, IL 61604, USA*

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ABSTRACT

A castor oil-derived diglycidyl ester plasticizer (C26-DGE) was prepared and incorporated into poly(vinyl chloride) (PVC) for the first time. The chemical structure of the product was characterized by Fourier transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance (^{1}H-NMR), and carbon-13 nuclear magnetic resonance (^{13}C-NMR). The plasticizing effects of C26-DGE as a primary or secondary plasticizer for the commercial plasticizer dioctyl phthalate (DOP) were studied. The mechanical properties, thermal stability, and migration stabilities of PVC films were investigated using dynamic mechanical analysis, thermogravimetric analysis (TGA), TGA-FTIR analysis, and PVC film surface analysis. Tensile, volatility, and extraction tests were also done. The castor oil-based plasticizer was found to endow the PVC matrix with enhanced compatibility and flexibility. With partially or completely substituted DOP, C26-DGE significantly increased the thermal stability of PVC blends. Furthermore, the volatility and extraction resistance of the novel plasticizers were generally superior to those of DOP. The interaction between the C26-DGE and PVC molecules and the thermal degradation process of PVC blends were also investigated.

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Address correspondence to E-mail: chenjie_hi@126.com; niexiaoan@126.com

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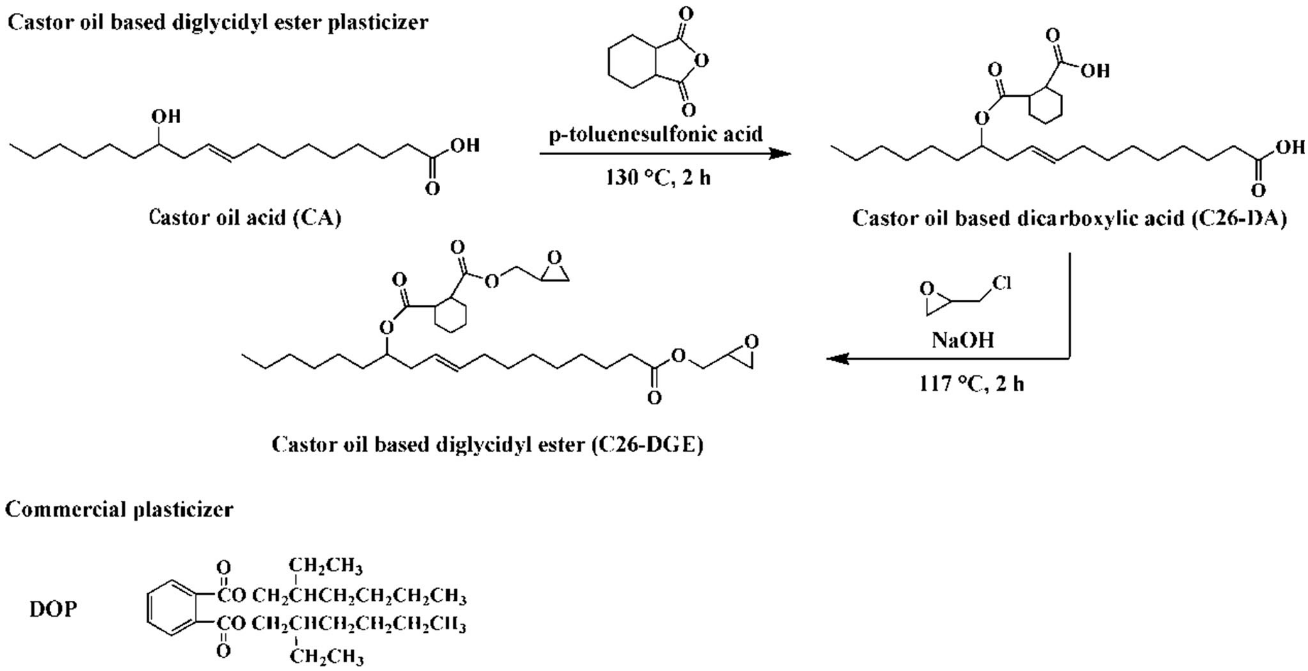


Figure 1 The design and synthetic routes of C26-DGE and the commercial plasticizer used in this study.

Introduction

Due to its high versatility and relatively low cost, PVC is one of the most common polymers in a wide range of applications [1]. Nevertheless, pure PVC has a high glass transition temperature (T_g), low thermal stability, and is rigid at room temperature [1–5]. Plasticizers (e.g., phthalates, phosphates, citrates, etc.) are employed to modify the flexibility and workability of PVC. Plasticizer molecules in filtrate the polymer matrix and find attractive forces within the polar groups of the PVC molecule [6–8]. These attractive forces decrease chain–chain interactions of the matrix and increase the free volume of the polymer amorphous region, decreasing T_g [7, 8].

In recent decades, plasticizers—particularly phthalate esters [i.e., DOP and dibutyl phthalate (DBP)]—have become controversial due to their migration phenomenon, bioaccumulation in the environment, and potential toxicity to humans [9–14]. Furthermore, the use of phthalates in PVC products such as toys, medical devices, and food packing has been gradually restricted in many countries [1]. Thus, researchers are paying increased attention to bio-based renewable plasticizers [15–19]. Plant oils represent a promising alternative for renewable plasticizers because of their improved biodegradability and low toxicity. Plant oil-based plasticizers include epoxidized oils and epoxidized fatty acid esters from soybean oil [20, 21], rubber seed oil [22], linseed oil [18], and sunflower oil [23].

Most of the major commercial plasticizers are esters, which allow specific polymer interactions (electrostatic, hydrogen bonds, or van der Waals) [1, 15]. The epoxy groups of the epoxidized plant oil-based plasticizers mentioned above can act as HCl scavengers and co-stabilizers to bring thermal stability to PVC [24]. The present work, therefore, means to develop a novel, plant oil-based plasticizer with esters acting as cohesive blocks and functional alicyclic and epoxy groups. Such a novel alternative plasticizer would offer outstanding thermal and migration stabilities as well as outstanding plasticizing effects.

In this work, a novel castor oil-based C26-DGE plasticizer has been synthesized (Fig. 1). Plasticizing properties such as dynamic mechanical properties, mechanical properties, and the thermal and migration stabilities of PVC films were researched and compared to those of DOP. The interaction between the C26-DGE and PVC molecules and the thermal degradation process of PVC blends were also investigated.

Experimental section

Materials

Castor oil fatty acid (97%), cyclohexanedicarboxylic anhydride (99%), dioctyl phthalate (99.5%), sodium hydroxide (97+%), epichlorohydrin (99%), benzyltriethylammonium chloride (97%), and *p*-toluenesulfonic acid (98%) were purchased from Aladdin Chemical Reagent Co., Ltd. (Shanghai, China). Zinc stearate and calcium stearate were provided by Changzhou Huaren Chemical Co., Ltd., (Changzhou, China). PVC (S-1000) was supplied by the Sinopec Qilu Co., Ltd., (Zibo, China).

Preparation of C26-DA

To a 100-mL flask equipped with a reflux condenser, thermometer and magnetic stirrer, castor oil acid (30.00 g), cyclohexanedicarboxylic anhydride (15.40 g), and p-toluenesulfonic acid (0.09 g) were charged. Then, the reaction was continued at 130 °C for 2 h. After cooling, the reaction mixture was soluble in ethyl acetate and washed with distilled water to neutral. Finally, the water was removed by distillation under vacuum at 80 °C. Then, the C26-DA was obtained.

Preparation of C26-DGE

C26-DA (20.00 g), benzyltriethyl ammonium chloride (0.32 g), and epichlorohydrin (85.00 g) were added to a flask equipped with amagnetic stirrer, thermometer, and reflux condenser. The reaction was continued at 117 °C for 2 h. After the reaction, the mixture was cooled to 60 °C, the sodium hydroxide (3.70 g) was charged. Then, the reaction was continued for 3 h at 60 °C. The mixture was separated by a Buchner funnel. Then, the excess epichlorophydrin in the filter liquor was recycled by distillation under vacuum. Finally, a yellowish liquid product was obtained. The acid value and epoxy value of the C26-DGE were 1.31 mg/g and 3.6%, respectively.

Preparation of PVC films

For comparison, pure PVC and plasticized PVC films with different plasticizers were prepared. Thermal stabilizers (Ca salts/Zn salts = 3/1), plasticizers and PVC were mixed by a mechanical mixer for 5 min at room temperature. Then, the blends were continuing mixed by double-roller blending rolls (Zhenggong Co., China) at 165 °C for 3 min. The PVC films with a thickness of 2 mm were obtained. The formulations are shown in Table 1.

Table 1 Formulation of the PVC films

Component (phr)	F0	F1	F2	F3	F4
Total plasticizer content	40.0	40.0	40.0	40.0	40.0
C26-DGE content	0.0	10.0	20.0	30.0	40.0
DOP content	40.0	30.0	20.0	10.0	0.0
Thermal stabilizers content	2.0	2.0	2.0	2.0	2.0

The FTIR measurements

The chemical structures of the plasticizer were confirmed by Fourier transform infrared (FTIR) spectra (Nicolet IS10 instrument, USA, KBr pellet) over a range of 4000–500 cm^{-1}.

Nuclear magnetic resonance

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

DMA measurement

Dynamic mechanical analysis (DMA) of the PVC films was studied on a DMA Q800 (TA Instruments, New Castle, DE) in a dual-cantilever mode at a frequency of 1 Hz. The testing was swept with a heating rate of 3 °C/min from − 60 to 80 °C. In order to ensure the reproducibility of data, replicated tests were carried out for each sample.

Measurement of mechanical properties

Tensile properties of the PVC films were measured through a SANS CMT-4303 universal testing machine (Shenzhen XinsansiJiliang Instrument Co., China) with cross-head speed of 10 mm/min, according to ISO 527-2: 1993. Each specimen was conditioned at 50% humidity and 23 °C for 1 day prior to tensile testing. To obtain an average value, five samples were tested for each group.

TGA analysis

Thermogravimetric analysis (TGA) was carried out on a 409PC thermogravimetric analyzer (Netzsch Co., Germany). The PVC films were heated from 40 to 600 °C at a rate of 10 °C/min under N_2 atmosphere.

TGA-FTIR analysis

The TGA-FTIR measurement was recorded on a NicoletiS10 FTIR (Nicolet Instrument Crop., USA) coupled with a 409PC thermal analyzer (Netzsch, Germany). Each PVC film was heated from 40 to 600 °C at a rate of 10 °C/min under N_2 atmosphere. The spectrum was collected within the range of 4000–500 cm^{-1} at a resolution of 4 cm^{-1}.

Volatility tests

Volatility tests were according to ISO 176:2005. The film with 120 cm^3 of activated carbon spreading over it was placed on the bottom of a metal container with lid. Then, the container was placed in the convection oven (Shanghai Suo pu Instrument Co., China) at 70 °C ± 1 °C. The container was removed from the oven and cooled in a desiccator after 24 h. The PVC film was brushed and reweighed. The weight loss was measured before and after the heating. To obtain an average value, three samples were tested.

Extraction tests

Extraction tests were according to ASTMD 1239-98. The PVC film was immersed in soybean oil, petroleum ether, distilled water, 10% (w/w) sodium hydroxide and 30% (w/v) acetic acid at 23 ± 1 °C and 50 ± 5% relative humidity. The extracted PVC film was rinsed by distilled water and wiped up after 24 h. Then, each film was dried in a convection oven (Shanghai Suo pu Instrument Co., China) for 24 h at 30 °C and reweighed. The weight loss before and after the immersing was measured. Three samples were tested to get an average value.

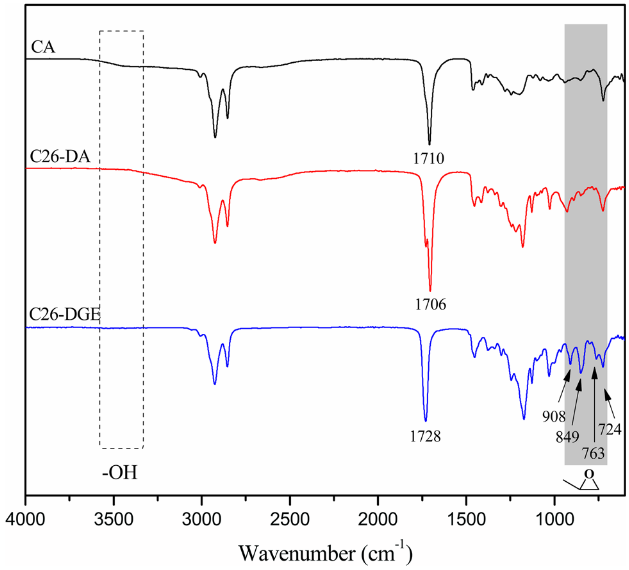


Figure 2 FTIR spectra of CA, C26-DA and C26-DGE.

Results and discussion

Synthesis and characterization

The FTIR spectra of CA, C26-DA, and C26-DGE are shown in Fig. 2. In the CA spectrum, the absorption peaks at 3550–3300 cm^{-1} were due to the presence of O–H stretching vibrations. The peak at 1710 cm^{-1} corresponded to the carboxylic acid group. Compared to the FTIR spectrum of CA, it can be seen that the absorption spectrum of the –OH group completely disappeared in the C26-DA spectrum. Furthermore, the strong peaks at around 1706 cm^{-1} corresponded to the double carboxylic acid groups. In the C26-DGE spectrum, the absorption at around 1728 cm^{-1} was attributed to carboxylic eater groups. Peaks of the glycidyl ester groups were observed at 908, 849, 763, and 724 cm^{-1}.The results indicate an epoxidation reaction of double carboxylic acid groups with epichlorohydrin.

The ^{1}HNMR and ^{13}C NMR spectra of C26-DA and C26-DGE are shown in Figs. 3 and 4. In Fig. 3a, the methyl protons are shown at around 0.90 ppm (peak 18). The methylene protons can be seen at around 1.32–1.39 ppm (peaks 4–7 and 13–17). The chemical shifts at around 1.43–1.81 ppm correspond to the methylene protons attached to a six-membered alicyclic ring and-CH_2COOH (peaks 20–23 and 3).The methylene group hydrogens attached to –COOH at 2.01 ppm. The chemical shifts around 2.24–2.38 ppm (peaks 8, 11, and 12) corresponded to the methylene

Figure 3 ^{1}H NMR spectra of **a** C26-DA and **b** C26-DGE.

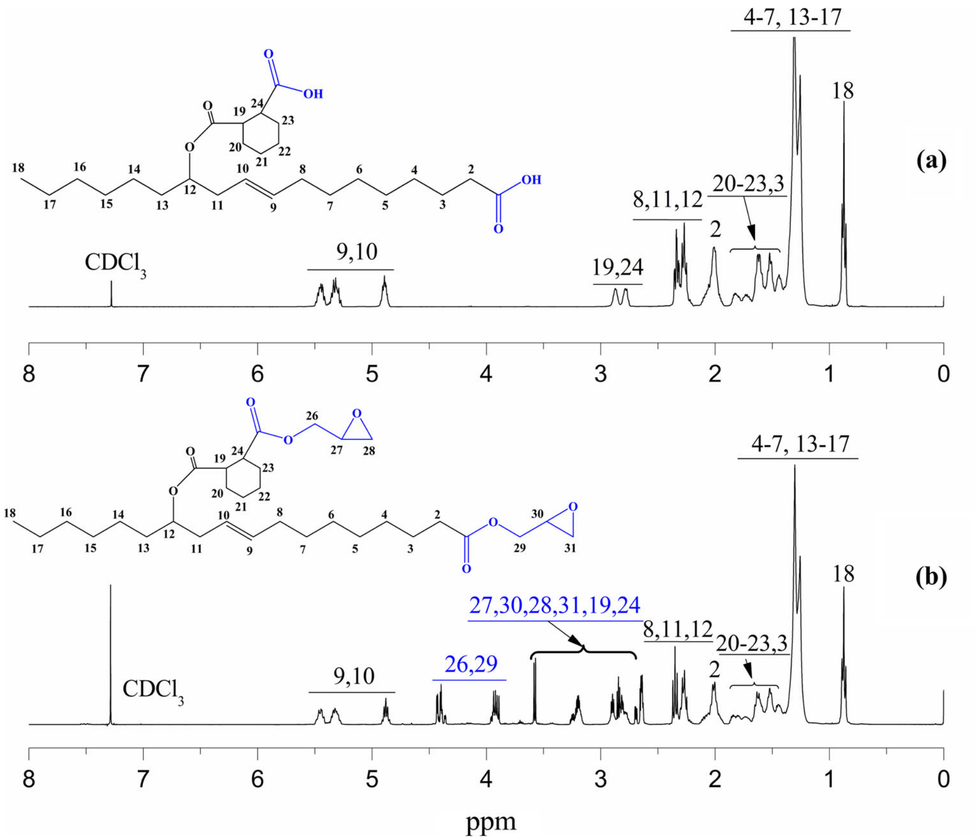
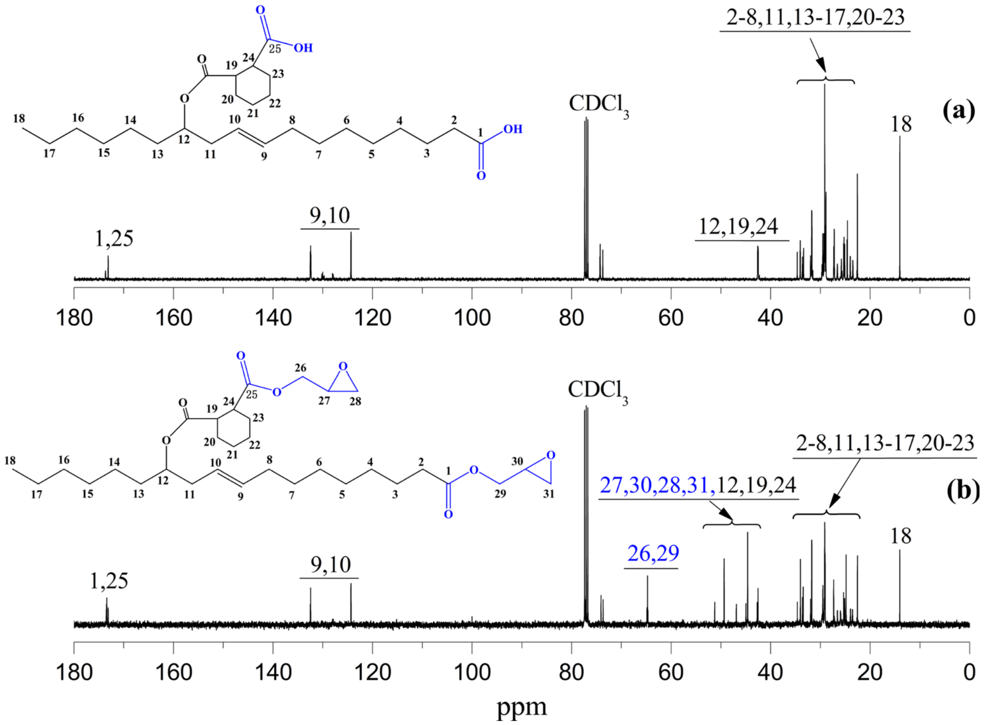


Figure 4 ^{13}C NMR spectra of **a** C26-DA and **b** C26-DGE.



and methyne associated with –CH=CH–. The methyne group protons attached to –O–O– and –C=O at 2.78 and 2.87 ppm. The peaks at around 4.89–5.45 ppm were attributed to the hydrogens of CH=CH (peaks 9 and 10). Proton signals at 2.63–4.41 ppm (peaks 26–31) and associated with the diglycidyl ester groups appeared in the spectrum (Fig. 2b), indicating an esterification reaction of C26-DA with epichlorohydrin. This result was in accordance with the FTIR results. Figure 4 shows the ^{13}C NMR spectra of C26-DA and C26-DGE. New peaks at 42.44–51.30 and 64.74 ppm (Fig. 4b) suggest the existence of glycidyl ester groups. The results indicate the successful preparation of C26-DGE.

Dynamic mechanical analysis

Dynamic mechanical analysis technology was employed to study pure PVC and the PVC films. In Fig. 5, a single peak is observed in each curve, suggesting homogeneity and good plasticizer compatibility with PVC [15, 25]. An important metric of plasticizing efficiency, glass transition temperature (T_g) is the temperature at the maximum of the tan δ curve. As shown in Table 2, the T_g values of films S0–S4 were 41.46, 34.85, 40.42, 44.46, and 47.55 °C, respectively—lower than that of pure PVC (92.29 °C). It can be seen that the T_g of films S1 and S2 (with 10 and 20 phrC26-DGE, respectively) are lower than that of film S0. An explanation for this can be seen in Fig. 6. The polar glycidyl ester groups and the six-membered alicyclic ring of C26-DGE interacted with the polar portion of the PVC molecule, while the long alkyl chain of C26-DGE lubricated the PVC matrix, increasing the free volume of the polymer amorphous region, resulting in a decrease in T_g. However, with increased C26-DGE content, the corresponding T_g increased. Because C26-DGE has a greater molecular weight (477.8) than DOP (391), the number of polar groups in the plasticizing system was relatively reduced, thereby decreasing PVC plasticity.

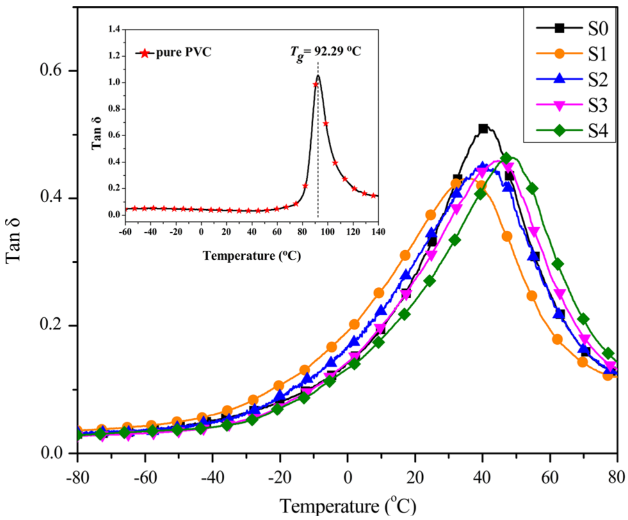


Figure 5 DMA curves for pure PVC and PVC films with different plasticizers.

Mechanical properties

Table 3 shows the tensile strength, elongation at break, and modulus of elasticity of the PVC films. It can be seen that PVC films plasticized with C26-DGE (films S0–S4) had similar tensile strength, better elongation at break, and a higher modulus of elasticity compared with film plasticized with pure DOP (film S0). The elongation at break of films S0–S4 generally increased from 210.7 to 310.6%, indicating a remarkable effect of C26-DGE on flexibility. This may be attributed primarily to lubrication of the PVC chains by the long alkyl chains ofC26-DGE. Lubrication reduces the polymer interaction force, increasing the free volume of the polymer amorphous region and potentially enhancing the flexibility of the PVC blends [26, 27]. It could be concluded that lower amounts of C26-DGE would be required to reach the same flexibility as is achieved with DOP.

Thermal stability

Figure 7 shows the TGA results for DOP and C26-DGE heated at 10 °C/min in nitrogen. The thermal degradation data, including the initial decomposition temperature (T_i) and 10 and 50% mass loss temperatures (T_{10} and T_{50}), are summarized in Table 2. Compared with DOP, the T_i, T_{10}, and T_{50} of C26-DGE increased 123.6, 94.1, and 141.4 °C, respectively. Hence, C26-DGE produced higher thermal stability, which might be attributed to the high thermal stability of the diglycidyl ester groups.

The thermogravimetric results for PVC films with varied C26-DGE content are shown in Fig. 8. Thermal data for T_i, T_{10}, and T_{50} weight loss at different times and residuals are summarized in Table 2. According to previous reports, two main degradation steps are observed in each TGA curve [28–30]. In the first stage, dehydrochlorination of PVC accelerated and the

Table 2 Thermal properties of PVC films with different plasticizers

Sample	T_g (°C)	T_i (°C)	T_{10} (°C)	T_{50} (°C)	Weight loss (wt%)	
					200–350 (°C)	400–550 (°C)
DOP	–	224.3	223.1	263.3	–	–
C26-DGE	–	347.9	317.2	404.7	–	–
S0	41.46	262.2	255.5	300.5	70.08	17.13
S1	34.85	264.1	262.1	302.1	66.94	17.74
S2	40.42	268.8	269.7	312.2	65.20	19.85
S3	44.46	267.1	272.2	314.7	63.02	21.00
S4	47.55	275.5	279.5	322.0	61.25	22.53

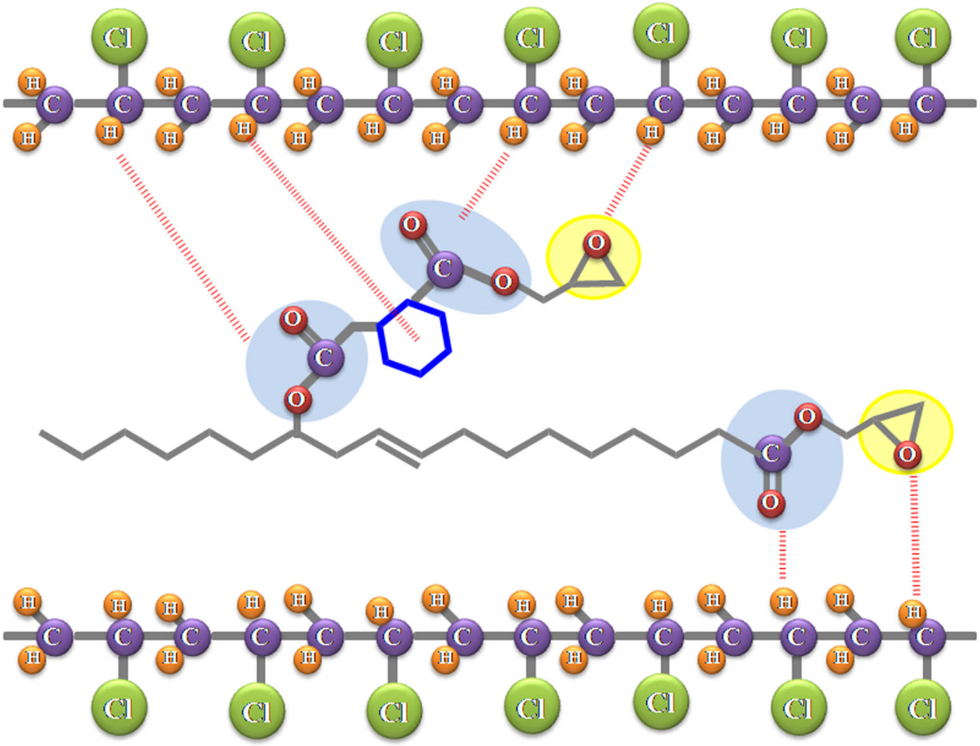


Figure 6 Schematic illustration of the interaction between C26-DGE and PVC molecule in the PVC matrix.

Table 3 Results obtained from tensile measurements

Sample	Tensile strength (MPa)	Elongation at break (%)	Modulus of elasticity (MPa)
S0	5.0 ± 0.084	210.7 ± 11.22	7.0 ± 3.27
S1	5.5 ± 0.26	242.5 ± 15.05	8.5 ± 1.12
S2	6.3 ± 0.40	244.8 ± 5.54	8.7 ± 4.91
S3	6.6 ± 0.22	256.3 ± 23.48	18.8 ± 1.37
S4	6.7 ± 0.31	310.60 ± 9.71	23.0 ± 1.33

greatest weight loss (70.08%) occurred between 200 and 350 °C. These cond degradation step were connected with the decomposition of the aromatic compounds (400–550 °C) and had the greatest weight loss 22.53% [31]. T_i, T_{10}, and T_{50} gradually increased when DOP was replaced with C26-DGE. When 30 phr DOP was substituted with C26-DGE, the T_i, T_{10}, and T_{50} were 4.9, 16.7, and 14.2 °C higher than S0, respectively. The film (S4) modified by 40 phr C26-DGE had the highest T_i, T_{10}, and T_{50} of 275.5, 279.5, and 322.0 °C, respectively. This finding is primarily due to the multi-glycidylester groups of C26-DGE which can react with HCl, delaying thermal decomposition

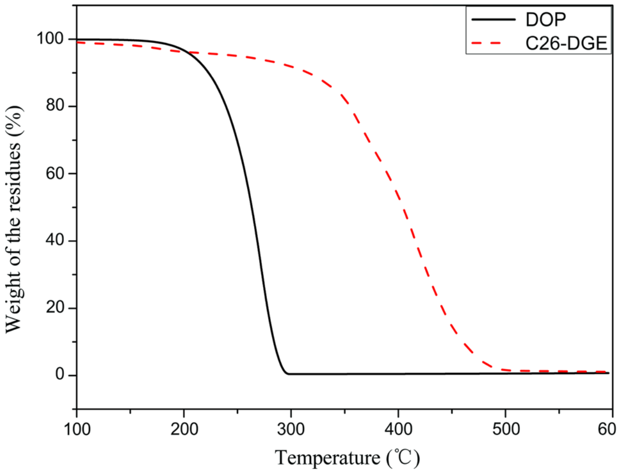


Figure 7 TGA curves of the plasticizers.

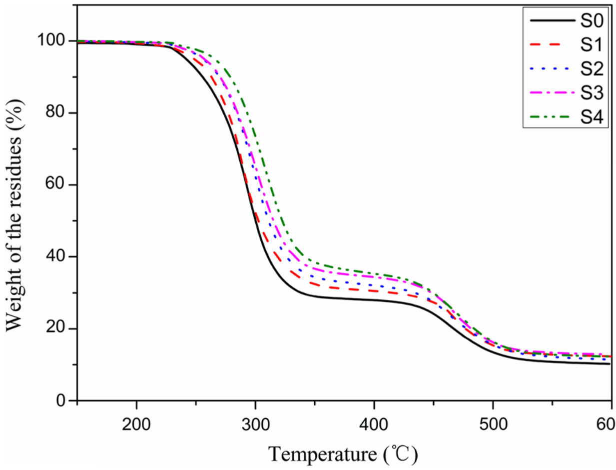


Figure 8 TGA curves of the PVC films with different plasticizers.

[32]. Hence, C26-DGE offers greater thermal stability in PVC blends than DOP.

The TGA-FTIR spectra of the gas products of the thermal degradation in the PVC films plasticized with DOP and C26-DGE are shown in Fig. 9a, b. The gaseous phases of the pyrolysis of films S0 and S4 were hydrogen chloride (HCl), water (H_2O), carbon dioxide (CO_2), carbon monoxide (CO), and benzene (C_6H_6); these were similar to one another. In the first degradation stage (at ~ 200–350 °C), the HCl (~ 2800 cm^{-1}), H_2O (3500–4000 cm^{-1}), and C_6H_6 (~ 3000 and 1500 cm^{-1}) were released [33, 34]. Figure 8b also showed that glycidylesters (1716, 1096, 802, and 668 cm^{-1}) were released due to the addition of C26-DGE. It is seen that more H_2O was obtained in the decomposition of film S4 than in film S0. Furthermore, with the incorporation of C26-DGE to PVC, a decline was observed in HCl concentration compared to that of pure DOP. However, the intensity of the absorption band of C_6H_6 in film S0 was higher than that of film S4, indicating that the addition of C26-DGE reduced C_6H_6 concentrations in PVC films during decomposition. These results were in agreement with the TGA results. Figure 10 shows the thermal degradation process of diglycidyl ester as a plasticizer for PVC. The ester groups, epoxy groups, and alicyclic structure of C26-DGE could, therefore, endow PVC with excellent thermal stability.

Surface characterization

The interaction between the plasticizers and PVC could be explored by FTIR according to the characteristic bands of the PVC matrix [35]. Figure 11 shows the FTIR spectra of the PVC films. In Fig. 11a, the peaks at 688 and 1426 cm^{-1} corresponded to the C–H and C–Cl of PVC, respectively [36]. As shown in Fig. 11b, c, obvious variations can be seen in the

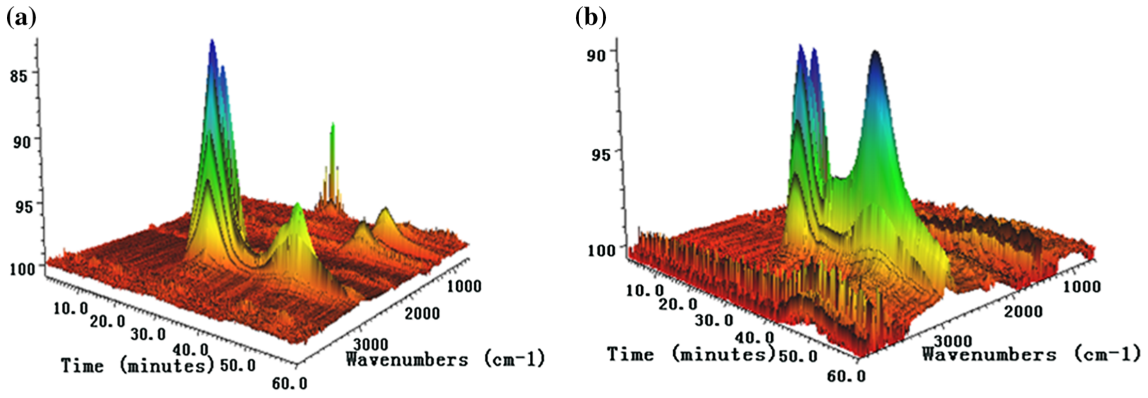


Figure 9 3D FTIR spectra of pyrolysis gas products of **a** film S0 and **b** film S4.

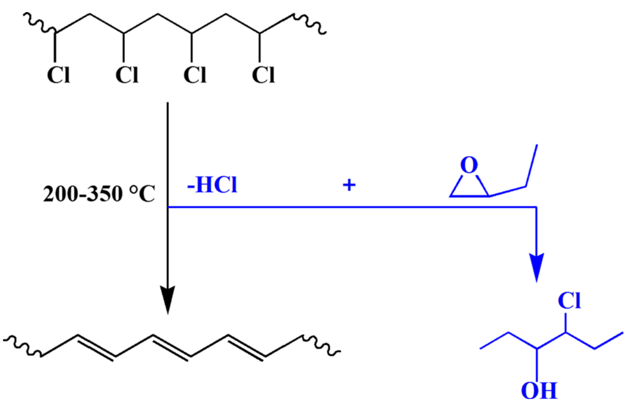


Figure 10 The process for the first thermal degradation stage of PVC with C26-DGE.

spectra of films S0–S4. The C–Cl and C–H absorption peaks visibly shifted toward the higher frequency at 1–5 cm^{-1}. This result could be explained by the relationship of the force constant to the vibration frequency through Hooke's Law [3] (Eq. (1)). The force constant increases with increased wave number, suggesting that the introduced electrons of the diglycidyl ester and carboxylic ester groups in the plasticizers formed hydrogen bonds with the –C–H– of the PVC molecules. Further, the finding indicated that the C26-DGE had a stronger interaction force with PVC than with DOP. This result is in agreement with the proposed plasticization mechanism shown in Fig. 6.

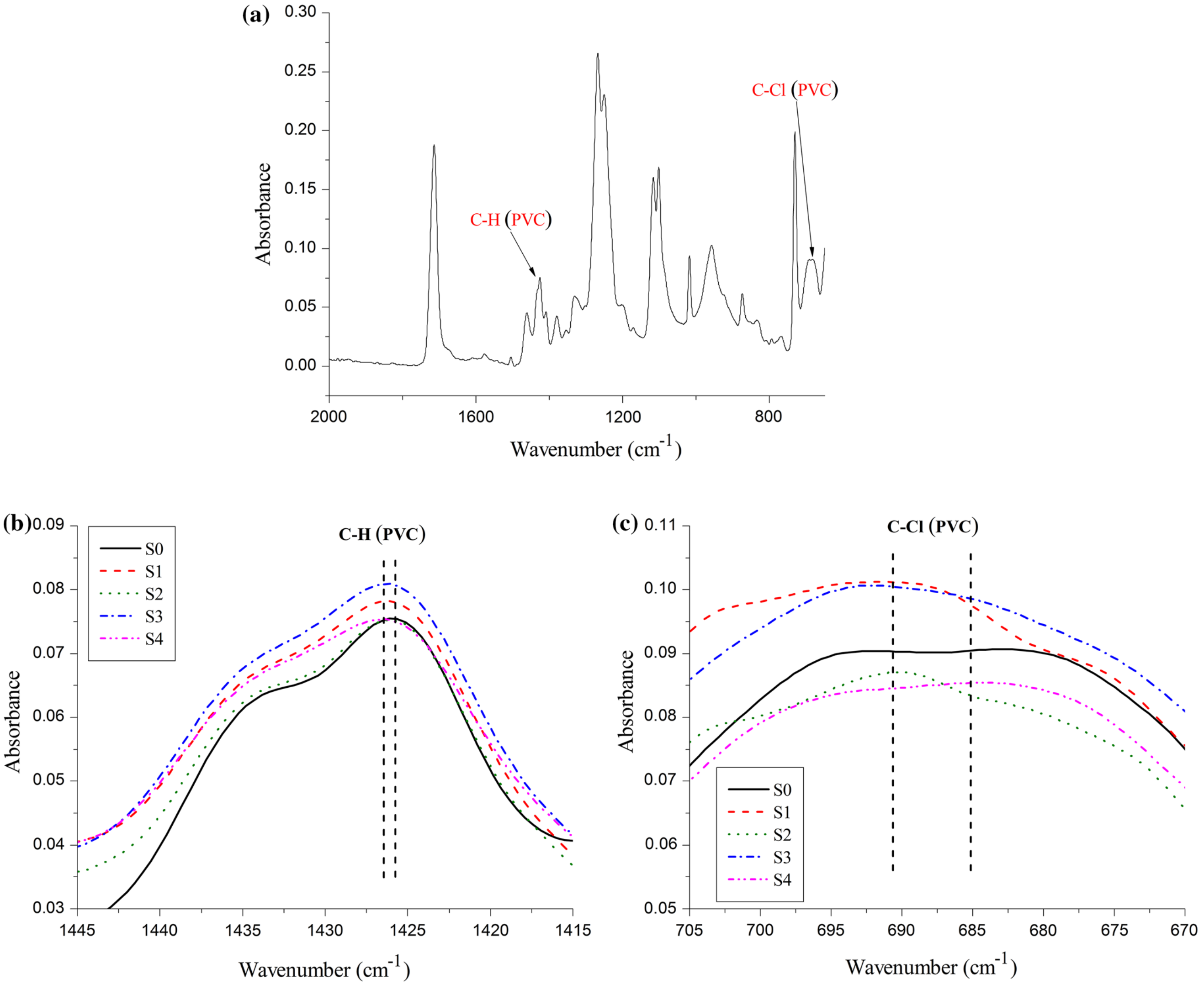


Figure 11 FTIR spectra of PVC films.

$$v = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \qquad (1)$$

where k is the force constant, v is the vibration frequency, and m is the mass.

Volatility and extraction resistance

Figure 12a shows weight loss in the PVC films following volatility testing. It can be seen that weight loss during volatility testing decreased in the order of F0, F1, F2, F3, and F4, suggesting volatilization loss generally declined with increased C26-DGE content. Figure 12b–f shows PVC film performance during extraction in petroleum ether, soybean oil, distilled water, 30% (w/w) acetic acid, and 10% (w/w) NaOH. The poorest resistance was observed in films leached in petroleum ether; this was attributed to the fact that the solvents were organic. Furthermore, it was clear that the migration resistance in soybean oil, 30% (w/w) acetic acid, and 10% (w/w) NaOH was improved when C26-DGE replaced DOP. The resistance of extraction by distilled water was similar to that of pure DOP. These results might be attributed to the chemical structure of the plasticizers [37] as well as to the intermolecular interactions between plasticizers and PVC.

Conclusions

A novel, renewable castor oil-based plasticizer (C26-DGE) was successfully prepared and applied to a PVC matrix. The plasticizing effects of C26-DGE partially or completely substituting for DOP were investigated. The results of DMA analysis and tensile tests indicated are markable increase in flexibility in PVC films plasticized with C26-DGE. The values of elongation at break of the PVC films (S0-S4) increased from 210.7 to 310.6%. When 10 and 20 phr DOP were replaced with C26-DGE, the T_g values decreased by 6.61 and 1.04 °C, respectively, compared to pure DOP. TGA and TGA-FTIR analyses suggested that C26-DGE could significantly increase the thermal stability of PVC blends. With 30 phr C26-DGE, the T_i, T_{10}, and T_{50} were 4.9, 16.7, and 14.2 °C higher, respectively, than those of DOP. The volatility and extraction tests showed that the migration stabilities of this plasticizer were mainly superior to those of DOP. The present study indicates that this castor oil-derived plasticizer is a promising alternative plasticizer for PVC and may be an excellent phthalate substitute in terms of human health and environmental protection.

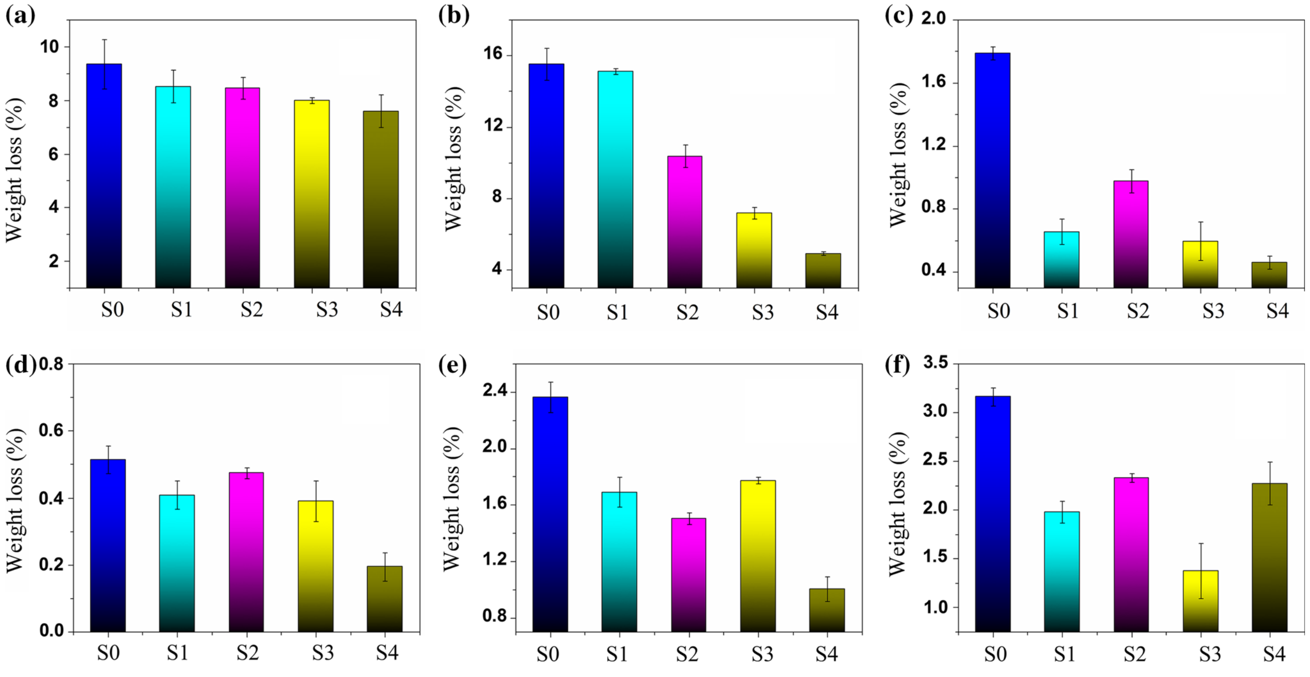


Figure 12 Weight losses of PVC films after volatilization and extraction testing: **a** volatility loss, **b** extraction loss in petroleum ether, **c** extraction loss in soybean oil, **d** extraction loss in distilled water, **e** extraction loss in 30% (w/v) acetic acid, **f** extraction loss in 10% (w/w) sodium hydroxide.

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Compliance with ethical standards

Conflict of interest The authors declare that there is no conflict of interests regarding the publication of this article.

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