Synthesis and Application of a Novel Epoxidized Plasticizer Based on Cardanol for Poly(vinyl chloride)

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ABSTRACT: Cardanol, an agricultural by-product of the industrial processing of cashew, was used to synthesize epoxidized cardanol laurate (ECDL) plasticizer. The target product was characterized using FTIR, ^{1}H NMR and ^{13}C NMR. The plasticizing effect of ECDL substitution for petroleum-based plasticizer dioctyl phthalate (DOP) in soft poly(vinyl chloride) (PVC) was investigated using dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA) and mechanical testing, and compared to PVC incorporated with commercial epoxidized soybean oil (ESBO). When DOP was partially substituted by EDCL, there was a slight increase of 5% in glass transition temperature (T_g) and a maximum increase of 14.55% in the elongation at break. In addition, scanning electron microscopy (SEM) revealed that the morphology of blends plasticized with DOP incorporated with ECDL was finer and more homogeneous compared with blends plasticized with neat DOP or ESBO. Compared with DOP/PVC, TGA results showed that the initial degradation temperature (T_i), the 50% weight loss temperature (T_{50}), and the first peak decomposition temperature (T_{p1}) for ECDL/PVC increased by 16.8, 26.5 and 7.1 °C, respectively. Moreover, plasticizing system with ECDL had longer stability time, lower volatility and exudation loss, and higher chemical resistance than that of DOP. Therefore, as an environmentally friendly and renewable biobased plasticizer, ECDL can partially replace DOP.

KEYWORDS: Plasticizer, epoxidized cardanol laurate, poly(vinyl chloride), plasticizing effect

1 INTRODUCTION

Plasticizers are additives used in polymer to render the material more flexible and malleable by forming dipole-dipole interactions with polymer chains [1, 2]. They are widely used in fields such as plastic toys, food packaging, medical pharmacology, wire and cable insulation, and automobile parts [3]. These additives are usually small molecules compared to large polymer chains, which make them more prone to migrate into the environment [4, 5]. The most commonly used plasticizers for PVC, including several phthalates, such as dioctyl phthalate (DOP), which is by far the most commonly used PVC plasticizer, are incontrovertibly becoming more limited due to their potentially toxic effects on human health and their environmental impact [6, 7]. For instance, DOP, dibutyl phthalate (DBP) and butyl benzyl phthalate (BBP) have been identified as being toxic to reproduction and have been restricted in the European Union for use in children's toys since 1999. Moreover, environmental concerns and petroleum shortages have encouraged extensive research on chemical products based on renewable resources [8, 9]. Because of their sustainability, ready availability and relatively low cost, there is a growing interest in the research and use of renewable raw materials [10]. Currently, some researchers have been reporting the synthesis and application of biobased plasticizer to replace phthalates, which mainly include epoxidized triglyceride oils, fatty acid esters, glycerol esters, and oleic acid polyester. Numerous raw materials have been used such as corn, soybean, palm, sunflower, and so on [11–14].

Cardanol, a phenol derivative bearing a C15 polyunsaturated side chain in the meta-position extracted from cashew nut shell liquid (CNSL), is a non-edible by-product of CNSL industries and is a promising aromatic renewable resource available in large quantities that would be suitable for food contact. With its reactive functional benzene ring, phenolic hydroxyl and unsaturated alkyl chain group, cardanol has been

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used in the preparation of many fine chemical products such as thermosetting resins, coatings and plasticizers [15–18]. Derivatives of cardanol have also been reported to be efficient plasticizers for PVC [19, 20]. Greco *et al.* [21] synthesized two different cardanol derivatives as renewable plasticizers for soft PVC, and results showed that cardanol acetate (CA) with PVC is partially miscible. However, further epoxidation yields complete miscibility with PVC. Chen *et al.* [22] synthesized glycidyl ether (CGE) from cardanol and compared it to the plasticizing effect of DOTP/PVC and DINP/PVC. The natural plasticizer CGE has good plasticizing efficiency, thermal stability and durability performance which compares to that of DOTP and DINP. Epoxides can be used directly as plasticizers that are compatible with PVC and as stabilizers for PVC resins to improve thermal stability. Moreover, the combination of rigid aromatic ring, long flexible alkyl chain and epoxy groups of the cardanol derivatives would impart unique performance to the PVC formulation.

In this work, epoxidized cardanol laurate (ECDL) was obtained by esterification of cardanol hydroxyl group and further epoxidation of double bonds in the side chain. Mechanical and dynamical properties of ECDL/PVC in the presence of DOP were evaluated and compared with the traditional vegetable oil plasticizer ESBO. Scanning electron microscopy (SEM) was used to observe the morphology of PVC blends after tensile testing, and thermogravimetric analysis (TGA) disclosed the degradation behavior. Soft PVC obtained by mixing DOP and ECDL showed good performance compared with PVC obtained by incorporating neat DOP. Therefore, ECDL can be used as a secondary plasticizer for PVC.

2 EXPERIMENTAL

2.1 Materials

Cardanol (CD, 89%), supplied by Shanghai Meidong Biomaterials Co., Ltd. (China), was refined under –0.8 to –1 bar at 240–270 °C. Poly(vinyl chloride) (PVC, S-1000) was obtained from Shandong Qilu Co., Ltd. (China). Dioctyl phthalate (DOP, 99%), epoxidized soybean oil (ESBO, 99%), lauric acid chloride and m-chloroperoxybenzoic acid (MCPBA, 75%) were obtained from Aladdin (China). Calcium stearate and zinc stearate were provided by Changzhou Jiarenhe Co., Ltd. (China).

2.2 Preparation

2.2.1 *Preparation of Cardanol Laurate (CDL)*

A mixture of CD (15.1 g, 0.05 mol), triethylamine (5 g, 0.05 mol) and 30 mL dichloromethane were put into a 100 mL three-necked round-bottom flask equipped with a mechanical stirrer, thermometer sensor and reflux condenser. Lauroyl chloride (14.2 g, 0.065 mol) was added dropwise over a period of 0.5 h and the reaction mixture was then continuously stirred in an ice bath. Under mechanical stirring, the reaction system was heated to 40 °C for 5 h. After the reaction was completed, the crude product was separated and subsequently washed with 5% sodium hydrocarbonate solution, saturated solution of sodium chloride and distilled water several times. Finally, the organic phase was dried with anhydrous magnesium sulfate overnight and filtered. The solvent was removed by a rotary evaporator and 22.87 g of a pale yellowish low-viscosity liquid was obtained (yield 94.45%).

2.2.2 *Preparation of Epoxidized Cardanol Laurate (ECDL)*

The CDL (14.6 g, 0.03 mol) was added into a 250 mL round-bottom flask which was equipped with a mechanical stirrer, thermometer sensor and reflux condenser. MCPBA (13.8 g, 0.06 mol) in 150 g dichloromethane was added into the flask slowly. The mixture was stirred at 30 °C for 3 h. Then the reaction mixture was refrigerated, filtered, and washed with sodium sulfite aqueous solution until the color of the potassium iodide-starch paper did not change. The mixture was neutralized and dried using the method above, and target product was obtained (yield 97%). Acid value of the resultant product was 1.2 mg/g KOH and epoxy value was 3.25%. The chemical reaction process of ECDL is shown in Figure 1.

2.3 Preparation of Plasticized PVC Test Films

The composition of PVC blends was a mixture of PVC, plasticizers and thermal stabilizers (calcium stearate/zinc stearate = 3:1) (Table 1). PVC blends were added into double-roller blending rolls at 165 °C for 5 min to make PVC films with thickness of 1 mm after being mixed thoroughly, which were used for the loss of volatility, exudation and migration tests.

2.4 Characterizations

2.4.1 *Fourier Transform Infrared (FTIR) Analysis*

The FTIR analyses of samples were conducted using a Nicolet IS10 spectroscope by an attenuated total reflectance method. The spectra were acquired in the range of 500–4000 cm^{-1} at a resolution of 4 cm^{-1}.

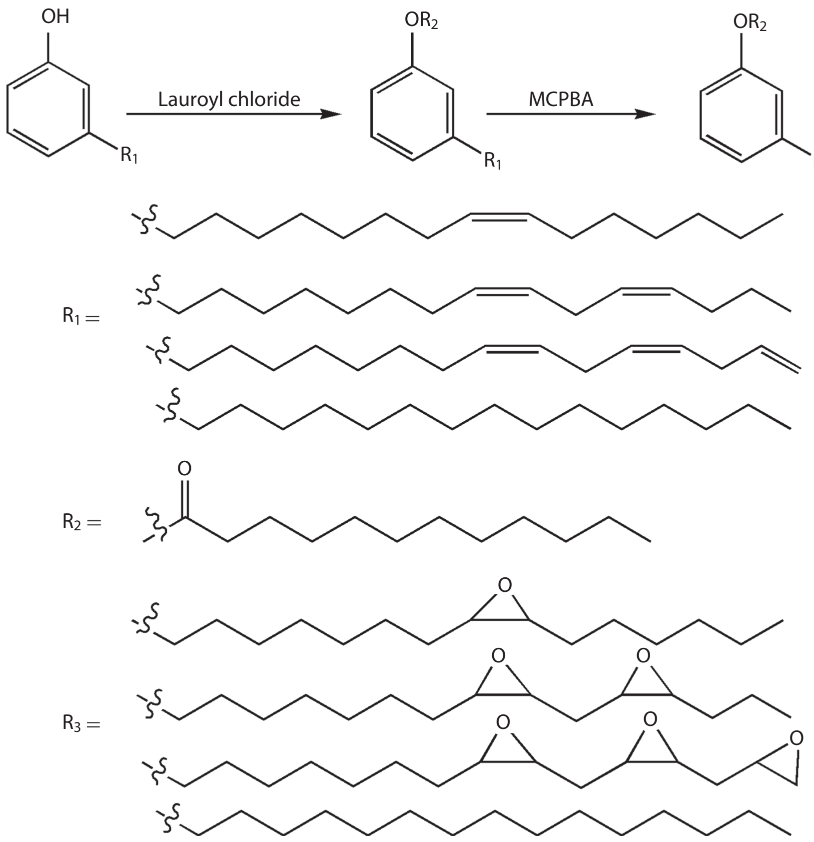

Figure 1 The synthesis route for ECDL.

Table 1 Composition of PVC blends.

Sample	PVC (g)	DOP (g)	ECDL (g)	ESBO (g)	Thermal stabilizer(g)
a	100	40	0	0	2
b	100	30	10	0	2
c	100	26.7	13.3	0	2
d	100	20	20	0	2
e	100	0	40	0	2
f	100	0	0	40	2

2.4.2 Nuclear Magnetic Resonance (NMR) Spectrum

The ^1H and ^{13}C NMR spectra were recorded with a Bruker AV300 at a frequency of 300 MHz. The chemical shifts were recorded in $CDCl_3$ with tetramethylsilane as an internal standard.

2.4.3 Dynamic Mechanical Analysis (DMA)

Samples were examined using DMA via a DMA Q800 (TA Co., USA) with a tensile test mode. The testing temperature was swept from −60 to 80 °C at a heating rate of 3 °C/min and a frequency of 1 Hz.

2.4.4 Thermogravimetric Analysis (TGA)

A 409PC thermogravimetric analyzer (Netzsch, Germany) was used to perform TGA. Each sample was scanned from ambient temperature to 600 °C under N_2 atmosphere at a heating rate of 10 °C/min. The mass of each sample was 5–10 mg.

2.4.5 Tensile Properties Measurement

Tensile properties were determined according to GB/T 1040.1-2006 under ambient conditions using a SANS CMT4303 universal testing machine (Shenzhen Xinsansi Jiliang Instrument, China). The tests were conducted at a drawing speed of 50 mm/min with a 30 kN static load cell. The test specimens assumed dumbbell shapes with a thickness of 0.2 mm, and five PVC specimens were prepared for each sample to obtain an average value.

2.4.6 *Scanning Electron Microscopy*

Analyses of the microstructure of tensile fracture surfaces were conducted on an S-3400N scanning electron microscope (Hitachi, Japan). The surfaces of fractured specimens were treated by spraying with gold before SEM observation.

2.4.7 *Torque Rheological Properties*

Evaluation of thermal stability and torque was carried out on a HAAKE PolyLab QC Rheometer according to ASTM D 2538-02. The PVC blends were tested at 180 °C with a rotor speed of 30 rpm for 150 min.

2.4.8 *Exudation, Volatility, and Extraction Tests*

Exudation tests of PVC films were evaluated by placing each film (20 mm × 20 mm × 1 mm) between two pieces of filter paper and placing them into a convection oven at 60 °C for 48 h. Then, the weight increases of filter papers were calculated.

Volatility tests of PVC films were measured by placing the films (20 mm × 20 mm × 1 mm) in a convection oven at 120 °C for 48 h. After cooling to room temperature, the weight changes before and after heating were measured.

Extraction tests were based on ASTM D 1239-98. The PVC films (20 mm × 20 mm × 1 mm) were immersed in distilled water, soybean oil, petroleum ether, cyclohexane at 23 ± 1 °C and 50 ± 5% relative humidity. After 24 h, the extracted PVC films were rinsed with flowing water and then wiped up. Once all of the films were dried in a convection oven at 30 °C for 24 h, they were reweighed. The weight losses before and after dipping were measured.

3 RESULTS AND DISCUSSION

3.1 Characterization of ECDL

The FTIR spectra of CD, CDL and ECDL are depicted in Figure 2. In the spectrum of CD, the absorption at 3344 cm^{-1} was attributed to stretching vibration of phenolic hydroxyl group. The absorption at 2926 and 2854 cm^{-1} corresponded to methyl and methylene groups. The absorption band at 1620–1450 cm^{-1} belonged to the C=C stretching vibration of aromatic ring and unsaturated alkyl chains [16]. The characteristic absorption of C-H in C=C was near 3008, 912 and 873 cm^{-1} [23]. In the FTIR spectrum of CDL, the characteristic absorption of ester groups at about 1763, 1228 and 1145 cm^{-1} were observed, while the absorption of phenolic hydroxyl at 3344 cm^{-1} disappeared. The results indicated CDL was successfully obtained. The FTIR spectrum of ECDL appeared for the characteristic absorption of epoxy group at 857 and 906 cm^{-1} [24, 25]. Whilst the absorption at 3008 cm^{-1} disappeared for ECDL compared with CD and CDL, implying double bond on the side chain was transformed to epoxy groups.

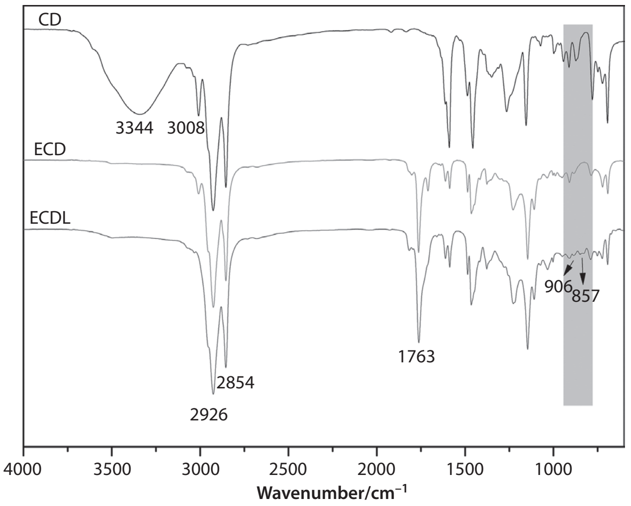

Figure 2 FTIR spectra of CD, CDL and ECDL.

The ^{1}H and ^{13}C NMR spectra of CD, CDL and ECDL are presented in Figures 3 and 4. In Figure 3, the peaks at 0.9–2.8 ppm corresponded to the methyl and methylene protons on alkyl chains of CD. The peaks at 5.3–5.6 ppm (peak i) were attributed to the double bond protons (-CH=CH-) of alkyl chain. The peaks at 6.8–7.3 ppm (peak c, d, b) represented the protons on the aromatic ring next to phenolic hydroxyl group. And the peak at 5.0 ppm is related to the proton of phenolic hydroxyl. In the ^{1}H NMR spectrum of CDL, the peak at 5.0 ppm almost disappears (the chemical shift of proton on terminal double bond was at about 4.9 ppm, which was close to the proton of phenolic hydroxyl, therefore some weak peaks still exist), while the peaks at 1.6 and 2.0 ppm appeared which were assigned to the other methylene by esterification reaction. Furthermore, the peak i disappeared and new peaks i′ and j′ at 2.52 and 1.55 ppm were ascribed to the protons on epoxy group, indicating the occurrence of epoxidation. In Figure 4, the peak at 13.6–35.5 ppm is associated with the methyl and methylene protons on alkyl chains. Compared with CD, a new peak appeared at 172.0 ppm assigned to the carbonyl group. In the ^{13}C NMR spectrum of ECDL, the peak i attached to double bonds disappeared and the peak i′ belonging

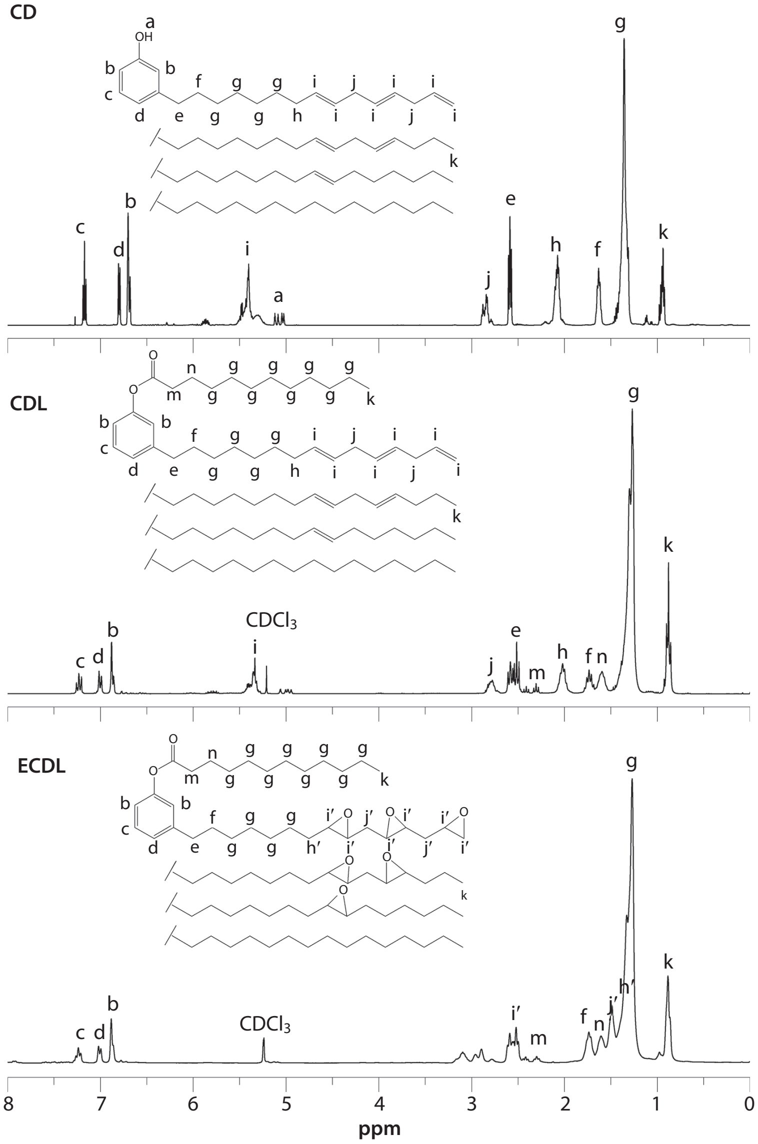

Figure 3 ^{1}H NMR spectra of CD, CDL, and ECDL.

to the epoxy group appeared, which implied that CD was successfully transferred into the target product.

3.2 Evaluation of PVC Blends

The DMA curves of PVC blends with different weight ratios are summarized in Figure 5. All tan δ curves displayed one glass transition temperature (T_g) corresponding to the curves' peak temperature, indicating that ECDL was compatible with PVC resin. With the content of ECDL increased from 0 to 20 g in PVC blends, T_g of PVC samples slightly increased from 38.78 to 40.80 °C. When the amount of DOP was completely substituted by ECDL, T_g of sample e was 49.25 °C. As is well known, T_g depends on the plasticizer's chemical structure and PVC blends' crosslinking state [26]. Because of a more rigid molecular structure and possibility of crosslinking at o, p positions on the aromatic ring, the applied force between plasticizer molecules and molecules of PVC becomes stronger and decreases the movement of PVC chain segments [27]. Compared with DOP/PVC, ESBO/PVC had an increase of 2.99 °C in T_g. And the molecules of ESBO had more epoxy groups and ester groups, which reduced PVC chain mobility [28, 29].

The thermal stability of PVC blends was characterized by TGA (Figures 6 and 7). The thermal degradation behavior of PVC plasticizing systems were compared by considering the initial decomposition temperature (T_i), the 50% weight loss temperature (T_{50}), the first

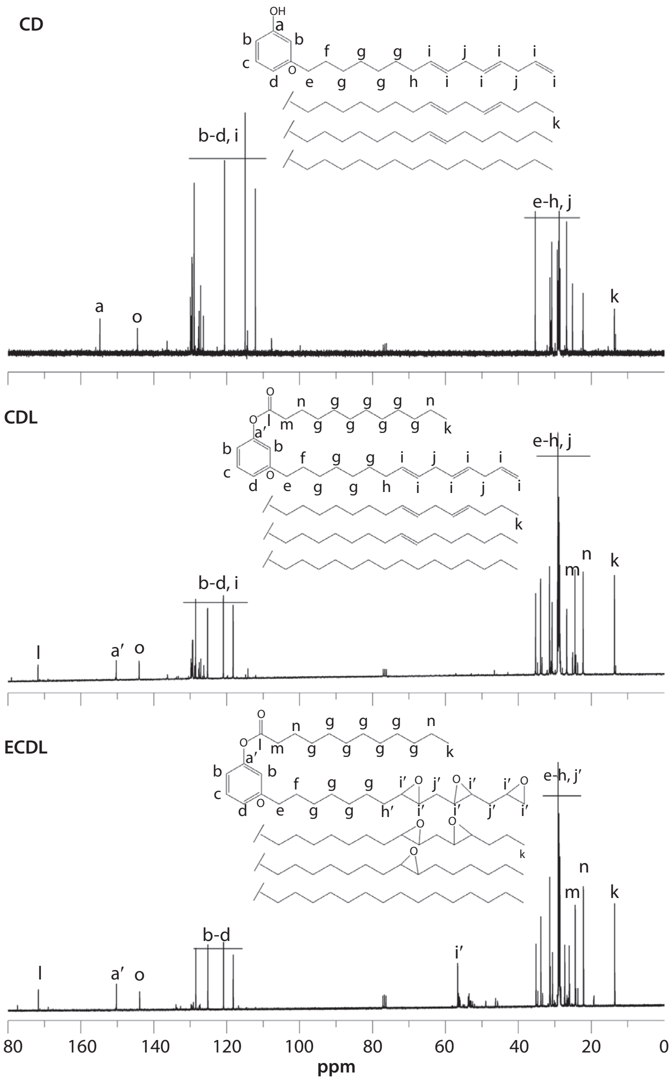

Figure 4 ^{13}C NMR spectra of CD, CDL, and ECDL.

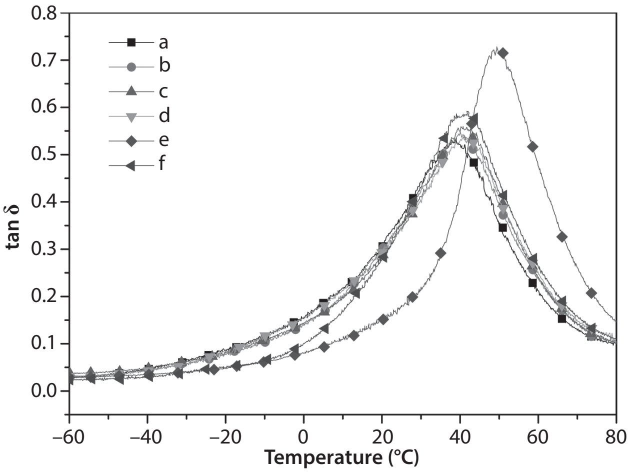

Figure 5 DMA curves of PVC blends with different weight ratios.

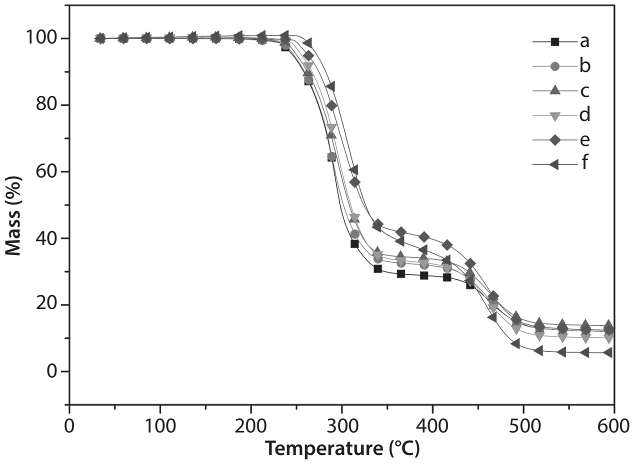

Figure 6 TGA curves of PVC blends.

peak decomposition temperature (T_{p1}), the second peak decomposition temperature (T_{p2}), and the char yield at 600 °C (Table 2).

From the TGA curves it can be seen that the thermal degradation processes occurred in two stages with varying mass rate losses. The first stage, which accounted for 60–70% of the weight loss, occurred at around 220–400 °C and was mainly due to dehydrochlorination forming conjugated polyene sequences. The second stage at above 400 °C was owing to aromatization of conjugated polyene sequences and further degradation of aromatic rings forming thickening rings as a part of char residue [30]. The DTG curves showed two distinct peaks at 290 °C and 460 °C, which corresponded to T_{p1} and T_{p2}. With the content of ECDL increased, T_i, T_{50} and T_{p1} of PVC blends had respective maximum increases of 16.8, 26.5 and 7.1 °C and T_{p2} showed little change (Table 2). The results indicated that ECDL had higher thermal stability than DOP. When DOP was replaced by ESBO, T_i, T_{50} and T_{p1} increased by 26.9, 28.4 and 15.8 °C, respectively, because epoxy groups in ECDL and ESBO can react with HCl generated by the degradation process and inhibit production of polyene sequences in the PVC chains. However, ESBO/PVC (sample f) had a lower mass residue than DOP and ECDL, because alkyl chains are easier to crack than aromatic groups [31, 32].

Mechanical properties of PVC blends are reported in Figure 8. With addition of ECDL and reduction of DOP in PVC blends, sample c had a maximum increase of 14.6% in the elongation at break. The elongation at break of plasticized PVC samples was 323.5, 349.6, 370.4, 356.7 and 307.4%, respectively, which illustrated that ECDL can be used as a secondary plasticizer with DOP, and the plasticizing efficiency was higher than DOP. The neat ESBO exhibited a percent elongation of 353.2%, which was much higher than that of sample a and lower than sample c. This was due to the presence of differing polarities and long-chain alkyls in ECDL, which supported the softening effect of PVC blends. With the content of ECDL increased, long alkyl chains in meta-position of ECDL would not be compatible with PVC due to the inherent polar nature of PVC chains.

Morphologies of PVC blends after tensile testing were investigated by SEM. Figure 9 displays the microstructure of tensile fracture surfaces of samples a, c, e and f. As shown in Figure 9a, there were some

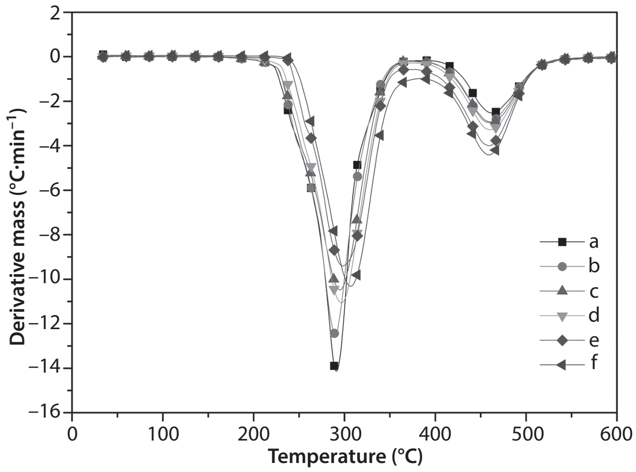

Figure 7 DTG curves of PVC blends.

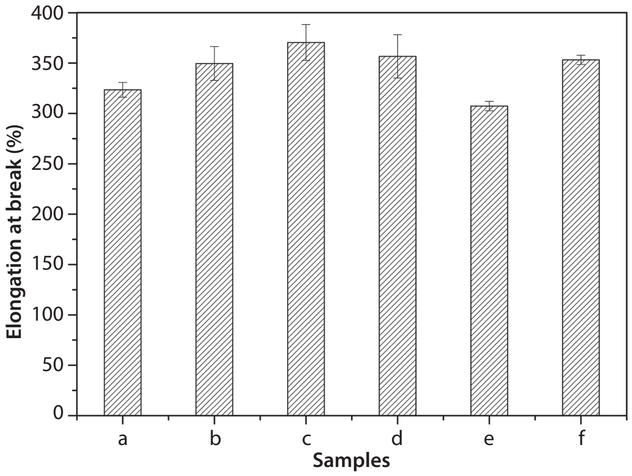

Figure 8 Tensile properties of PVC samples.

Table 2 TGA results of PVC blends.

Sample	T_g (°C)	T_i (°C)	T_{50} (°C)	T_{p1} (°C)	T_{p2} (°C)	Char yield (%)
a	38.78	245.9	297.8	291.0	461.9	12.03
b	39.87	247.2	301.7	290.0	459.2	12.07
c	40.60	250.5	307.9	295.1	461.6	13.82
d	40.80	255.5	309.9	296.9	460.5	10.12
e	49.25	262.7	324.3	298.1	459.6	12.38
f	41.77	272.8	326.2	306.8	458.9	5.67

textures and particles in PVC film plasticized by DOP. However, a compatible phase was observed and more obvious grains were seen in the fractured surface of sample c which provided good mechanical properties. This observation indicated that the addition of ECDL improved the dispersion state of PVC blends. With increasing EDCL content, there were still some particles and aggregates on the fractured surface, meaning that excess ECDL can negatively affect mechanical properties. This was probably due to the molecular weight of ECDL (508) being greater than that of DOP (390), so the average content of polar groups (ester group and epoxy group) in PVC blends decreased for the amount of plasticizer within blends determined by weight, and not by moles [33]. As shown in Figure 9f, the fracture surface of sample f was similar to sample c, which indicated a homogeneous phase was formed. The results were in agreement with the mechanical properties.

To verify dynamic stability, processing data were collected (Figure 10). Compared with DOP/PVC, the stability time of ECDL/PVC was prolonged from 12.22 to 44.72 min, and balanced torque increased from 3.0 to 4.7 N·m. PVC sample of ESBO/PVC had longer stability time and larger balance torque due to more epoxy groups existing in ESBO. All of the results indicated that ECDL can partly substitute DOP to improve processability of PVC by extending the processing time [34]. These results were consistent with the TGA data which implied that ECDL increased the thermal stability of PVC blends.

After soaking in a high temperature environment for a long time, small molecules of plasticizer will migrate to the surface and evaporate from inside PVC material, which influenced the stability of PVC material performance. Figure 11 shows the mass losses of PVC blends by volatility and exudation. It can be seen that over the entire composition range studied, the

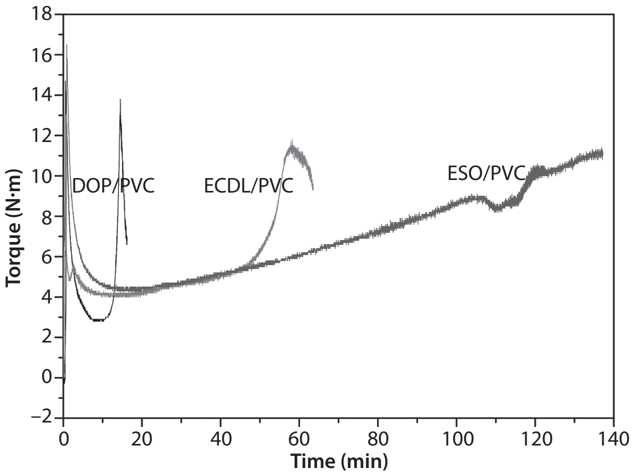

Figure 10 Dynamic thermal stability of PVC blends with different plasticizers.

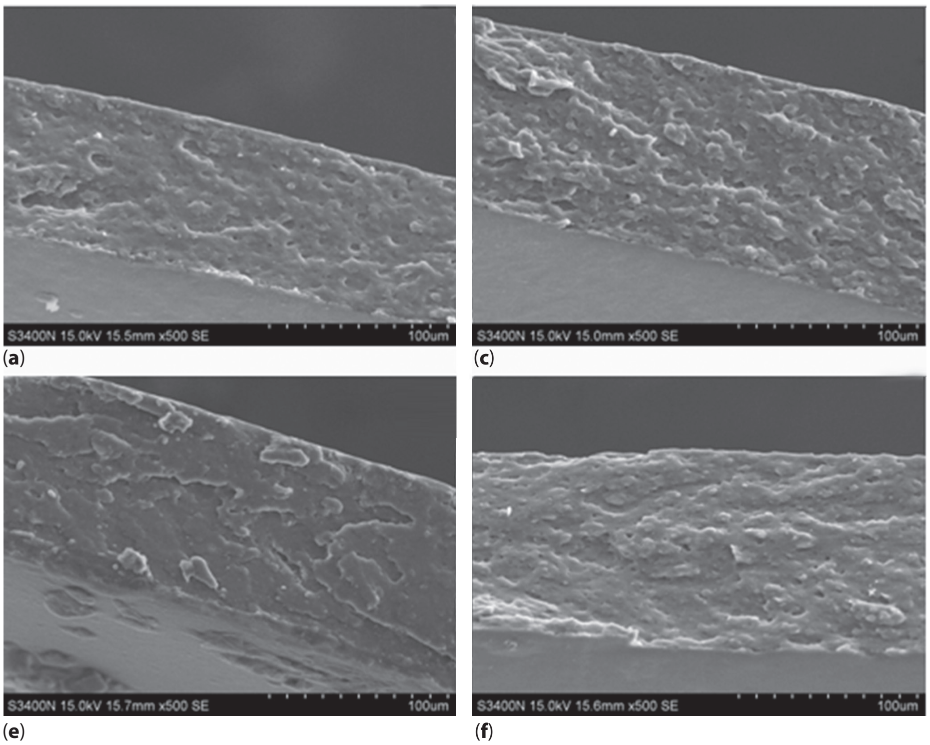

Figure 9 SEM micrographs of fractured surface of PVC sample (**a**), (**c**), (**e**), and (**f**).

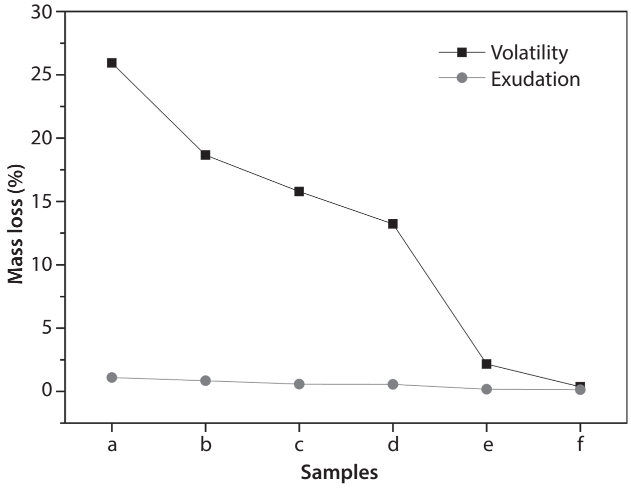

Figure 11 Mass losses of PVC samples after volatility and exudation tests.

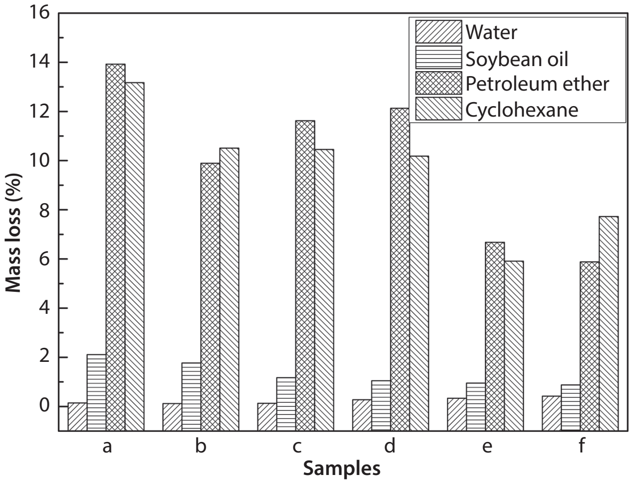

Figure 12 Migration loss of PVC blends in different solvents.

volatility loss decreased significantly in comparison to DOP. The differences between DOP and ECDL can probably be attributed to the stronger intermolecular interactions between PVC and long chains or epoxy groups of ECDL in comparison with short aliphatic chains of DOP. When DOP was partially or totally substituted by ECDL, epoxy group in the plasticizer chain scavenged HCl molecules released by the decomposition process. Therefore, it prevented the degradation of PVC resin from dehydrochlorination [35, 36]. All of the blends presented similar small exudation losses.

Figure 12 shows the migration losses of PVC blends studied in water, soybean oil, petroleum ether and cyclohexane, respectively. It was clear that the chemical resistance of PVC blends had a decreasing tendency in different solvents with increasing ECDL content. The PVC blends were almost unaffected by water, and the exposure of PVC blends to solvents like soybean oil, petroleum ether, and cyclohexane, resulted in less change than that for pure DOP. This behavior might be attributed to the larger molecular weight and epoxy group of ECDL. Thus, blends containing ECDL were more resistant towards solvents than blends with pure DOP.

4 CONCLUSIONS

A novel plasticizer ECDL based on cardanol was successfully synthesized by esterification and epoxidation reaction. This additive was then used in soft PVC incorporated with DOP. The plasticizing effects of PVC blends were mainly characterized by DMA, TGA, mechanical properties, SEM and dynamic stability, and these were compared with commercial epoxy plasticizer ESBO. DMA, mechanical properties and SEM analysis showed that when the content of ECDL was 33.3% (the total weight of plasticizer), PVC blend had the best compatibility and plasticizing performance. Moreover, thermal stability of PVC blends was increased with the addition of ECDL due to the existence of epoxy group. The PVC blends were further studied through volatility test, exudation test and chemical resistance, which disclosed that ECDL also had good migration resistance. Therefore, ECDL has the potential to be an alternative to petroleum-based plasticizers and reduce the harmful effects that phthalates have on humans and the environment.

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