

Synthesis and application of a natural plasticizer based on cardanol for poly(vinyl chloride)

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ABSTRACT: A natural plasticizer with multifunctional groups, similar in structure to phthalates, cardanol derivatives glycidyl ether (CGE) was synthesized from cardanol by a two-step modification process and characterized by FT-IR, ¹HNMR, and ¹³CNMR. The resulting product was incorporated to PVC (CGE/PVC), and plasticizing effect was compared with PVC incorporated with two kinds of commercial phthalate ester plasticizers bis (2-ethylhexyl) benzene-1,4-dicarboxylate (DOTP) and diisononyl phthalate (DINP). Dynamic mechanical analysis and mechanical properties testing of the plasticized PVC samples were performed in order to evaluate their flexibility, compatibility, and plasticizing efficiency. SEM was employed to produce fractured surface morphology. Thermogravimetric analysis and discoloration tests were used to characterize the thermal stabilities. Dynamic stability analysis was used to test the processability of formulations. Compared with DOTP and DINP plasticized samples, CGE/PVC has a maximum decrease of 9.27% in glass transition temperature (T_g), a maximum increase of 17.6% in the elongation at break, and a maximum increase of 31.59°C and 25.31 min in 50% weight loss (T50) and dynamic stability time, respectively. The obtained CGE also has slightly lower volatility resistance and higher exudation resistance than that of DOTP and DINP. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42465.

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INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the five general synthetic resins and owes its wide utility to its high versatility, unique among high-volume thermoplastic addition polymers, to accommodate many different additives at many different loading levels.^{1–4} As the most consumable additives in PVC, plasticizers are an important class of low molecular weight nonvolatile compounds.¹ These substances usually reduce the second-order transition temperature, the glass transition temperature (T_g), the elastic modulus, tension of deformation, density, hardness, viscosity and electrostatic charge of a polymer, simultaneously increasing the polymer chain flexibility, processing properties, resistance to fracture, and dielectric constant.⁵ Furthermore, other properties of the polymer like degree of crystallinity, optical clarity, electric conductivity, fire, and biological degradation resistance are also affected.⁴

There are presently around 300 plasticizers which are manufactured and perhaps 100 which are of commercial importance,

among which phthalates play an important role and account for more than 80% due to their good performance and low price.⁶ However, according to recent reports, phthalates have demonstrated toxicity in animals and high risk of adverse health effects on humans.^{7–10} Thus, the use of plasticizers is being questioned. In accordance with this trend, there is an increasing interest in the use of natural-based plasticizers that are characterized by low toxicity for substitution of conventional petroleum-based plasticizers.^{5,11–14} Therefore, research into the replacement of petroleum-based plasticizers for renewable plasticizers has caught the attention of researchers in academia and industry.^{15,16}

Cashewnut shell liquid (CNSL) is one of the most commonly used renewable agricultural resource materials.¹⁷ As an extracted product from CNSL, cardanol (CD) and its derivatives have major applications in synthetic resin,¹⁸ epoxy curing agents,¹⁹ coatings,²⁰ biocomposites,^{21–23} and antioxidants,²⁴ taking advantage of its versatile chemical structure and high chemical reactivity. Since CD presents chemical and physical properties

very close to those of dioctylphthalate (DEHP), recently CD has been used as plasticizers in polymer and rubber industries with or without modification, and has shown significant plasticizing effects.^{5,25} On the other hand, CD and its derivatives have also been proved to be efficient plasticizers for PVC, although not much research has been reported.^{26,27} Considering the terminal epoxy groups have better behavior on plasticizing effects and thermal stabilities of PVC than the internal oxiranes, it was expected that the CD derivative containing a main chemical structure similar to DEHP and an extra polar terminal epoxy group might be a potential plasticizer of PVC.

In this work, cardanol derivatives glycidyl ether (CGE) was obtained by a two-step modification process²⁸ and is used as a plasticizer in PVC for the first time. Moreover, mechanical and physical characterizations, thermal behaviors, and processing properties were studied. For comparison, two kinds of commercial phthalate plasticizers bis(2-ethylhexyl) benzene-1,4-dicarboxylate (DOTP) and diisononyl phthalate (DINP) were also evaluated in PVC plasticization. The objective of this work is to demonstrate that the glycidyl ether derived from CD can offer better plasticizing effects than commercial phthalate plasticizers in PVC plasticization.

EXPERIMENTAL

Materials

CD (stabilized, 88.5%) was purchased from Shanghai Meidong Biological Material Co., Ltd., China. The refractive index (n_D^{25}) of CD is 1.509, viscosity is 46 mPa s (25°C), density is 0.928 g/cm³ (25°C). CD was used after distillation. Epichlorohydrin, sodium hydroxide (98.7%), calcium oxide (98%), and benzyltriethylammonium chloride (97%) were purchased from Sinopharm Chemical Reagent Co., Ltd., China and used as received. PVC (DG-1000K) was purchased from the Tianjin Dagu Chemical Co., Ltd, China. Calcium stearate and zinc stearate were supplied by Changzhou JiaRenWo Chemical Co., Ltd, China. Di (2-ethylhexyl) phthalate (DOTP) (97%) and DINP (99%) were obtained from Aladdin Chemical Reagent Co., Ltd., China, and were used as received.

PREPARATION

Preparation of CGE

CD (300 g) was charged into a flask equipped with a fractional distillation device. The temperature and vacuum were raised to 240.0–260.0°C and 8 Torr, respectively. A pale yellow distillate was obtained and had a CD purity of 98.5%. To a 250 mL flask equipped with mechanical stirrer, reflux condenser and thermometer were charged 50.0 g (0.166 mol) of CD, 122.5 g (1.32 mol) of epichlorohydrin, and 0.9 g (0.00485 mol) benzyltriethyl ammonium chloride. The final mixture was slowly heated to 95°C and kept reacting for 2.5 h. After the mixture was cooled to 60°C, 6.64 g (0.166 mol) sodium hydroxide and 12.30 g (0.166 mmol) calcium oxide were charged. Then the reaction was continued at 60°C for 3 h. The excess epichlorohydrin was distilled to be recycled and the solids were filtered. 55.52 g of a yellowish low-viscosity compound was obtained (yield: 93.05% relative to CD). The viscosity of CGE is 22 mPa s (25°C) and its epoxy value is 4.42%.

Table I. PVC Formulations for Varying Plasticizer Content

Component	Formulations		
	CGE/PVC	DOTP/PVC	DINP/PVC
PVC	100.00	100.00	100.00
CGE	25.00	0.00	0.00
DOTP	0.00	25.00	0.00
DINP	0.00	0.00	25.00
Calcium stearate	1.50	1.50	1.50
Zinc stearate	0.50	0.50	0.50

Preparation of Plasticized PVC Test Specimens

A series of plasticized PVC test specimens with different plasticizers were prepared. The compositions of different formulas are shown in Table I. First, PVC powder, plasticizer, and thermal stabilizers were mixed using a mechanical mixer at room temperature (RT) for 10 min. Then the mixture was compounded into a homogeneous mixture at 165°C for 3 min by a Haake torque rheometer (Thermo Fisher Scientific Inc., USA). The test specimens were made using a HAAKE MiniJet II micro injection molding machine (Thermo Fisher Scientific Inc., USA). The mold for tensile test samples is based on ISO527-2-5A with the dimensions of 75 mm × 12.5 mm × 2 mm. And the mold for dynamic mechanical analysis (DMA) samples is based on ISO180/179 with the dimensions of 80 mm × 10 mm × 4 mm. The specimens were carefully removed from the mold and examined for tensile test and DMA.

Characterizations

Fourier transform infrared (FTIR) analysis was conducted using a Nicolet IS10 spectroscopy (Thermo Fisher Scientific Inc., USA) by an attenuated total reflectance method. The samples were scanned from 4000 to 500 cm⁻¹. ¹H and ¹³C nuclear magnetic resonance (NMR), spectra of the compounds in deuterated chloroform (CDCl₃) were recorded on a Bruker ARX 300 spectrometer (Bruker Co., Germany) at RT.

DMA was measured by using a DMA Q800 (TA Co., USA) in a dual cantilever mode with a frequency of 1 Hz. The testing temperature was swept from -60 to 80°C at a heating rate of 3°C/min. For each sample, replicated tests were performed in order to ensure the reproducibility of data.

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 samples were conditioned at 23°C for 1 day prior to tensile testing. Five sample pieces were prepared for each group to obtain an average value. The Shore A durometer hardness was determined according to ASTM D2240.²⁹ Five measures at 15 s per sample were performed.

Scanning electron microscopy (SEM) examinations of the stretch-fractured samples were conducted on an S-3400N Scanning Electron Microscope (HITACHI Co., Japan). The surface of the fractured samples after completion of the tensile tests was coated with a gold film prior to SEM observation.

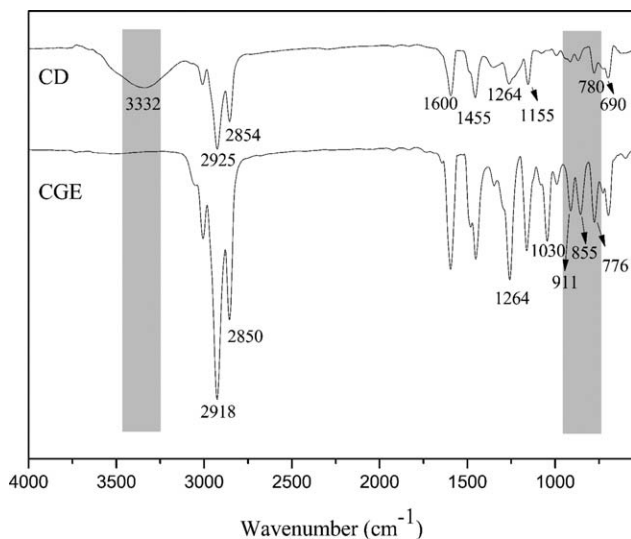


Figure 1. FT-IR spectra of CD and CGE.

Thermogravimetric analysis (TGA) was carried out in a thermogravimetric analyzer (Netzsch Co., Germany). Each sample was scanned from ambient temperature to 600°C under a nitrogen atmosphere at a heating rate of 10°C/min.

Static thermal stability analysis was performed according to the ISO 305:1990 (E). The PVC sample with a thickness of 1 mm was cut into a square with a length of 15 mm, and then was placed into the aging oven (Shanghai Sanfa Instrument Co., China) at 185°C. One strip was removed every 10 min. The static thermal stability of the sample was evaluated by comparison of color change in the heated PVC strips. For each sample, duplicated tests were performed in order to ensure the reproducibility of data.

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.³⁰

Volatility Properties were placed in a convection oven (Shanghai Suopu Instrument Co., China) at 70°C for 48 h and cooled to RT in a desiccator for 2 h. The weight changes were measured before and after the heating. The PVC films were 20 mm × 20 mm × 1 mm.

Exudation Properties of the plasticizer was evaluated by placing a sample (20 mm × 20 mm × 1 mm) between two pieces of filter paper. These systems were then placed in a convection oven (Shanghai Suopu Instrument Co., China) at 30°C for 48 h. The weights of the films were measured after washing the surfaces of the films with acetone and drying at RT. The weight changes before and after washing were calculated.

RESULTS AND DISCUSSION

Characterization of CGE

FT-IR technique was employed to study the structure of modified CD. The FT-IR spectra of CD and CGE are depicted in

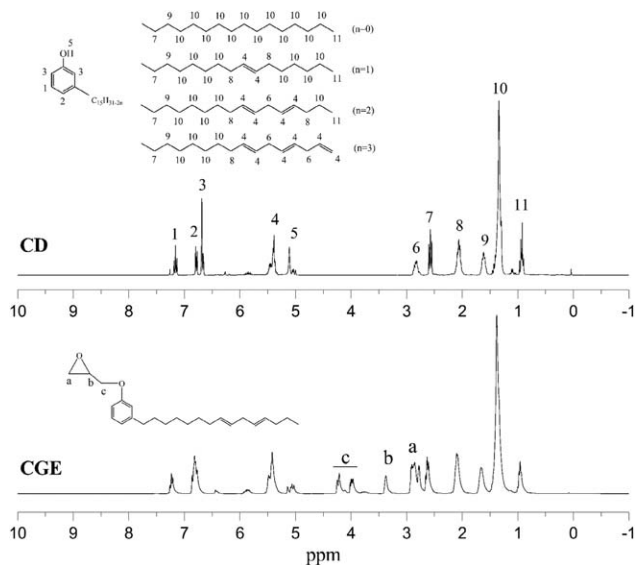


Figure 2. ¹H NMR spectra of CD and CGE.

Figure 1. In the spectrum of CD, there are several typical peaks: the phenolic hydroxyl group (3332 and 1350 cm^{-1}), C—H in —CH=CH— on benzene ring and unsaturated alkyl chains (3009 and 970 cm^{-1}), methyl, methylene and methine groups (2925, 2854, and 1455 cm^{-1}), C=C on aromatic ring (1600 cm^{-1}), symmetric and asymmetric stretching of C=C (1264 cm^{-1} , 1155 cm^{-1}), vibration of the four hydrogen atoms adjacent to the benzene ring (780 cm^{-1} , 690 cm^{-1}).³¹ In the spectrum of CGE, there are also some characteristic peaks: methyl and methylene (2918 and 2850 cm^{-1}), ether group (777–911 cm^{-1}), C—H in —CH=CH— on benzene ring and unsaturated alkyl chains (3006 cm^{-1}). And three obvious changes have been found in the spectrum of CGE. First, the typical peak of phenolic hydroxyl group at 3332 cm^{-1} is not observed. Second, characteristic features of ether group are found at 776, 855, and 911 cm^{-1} . Third, new peaks appear at 1264 and 1030 m^{-1} due

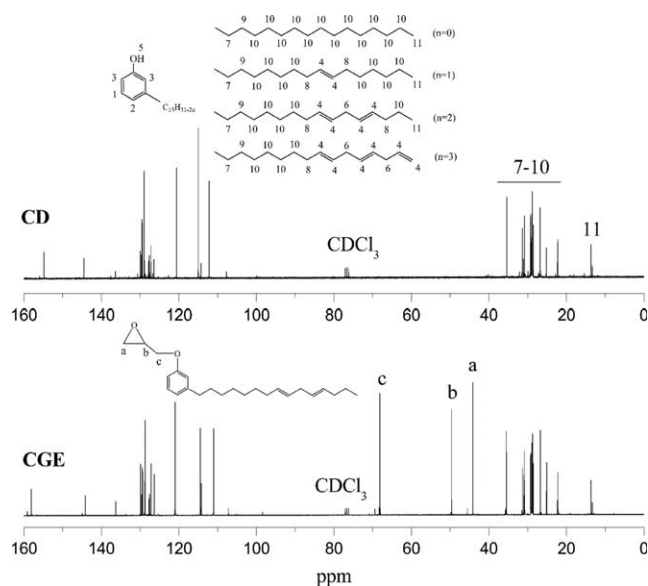


Figure 3. ¹³C NMR spectra of CD and CGE.

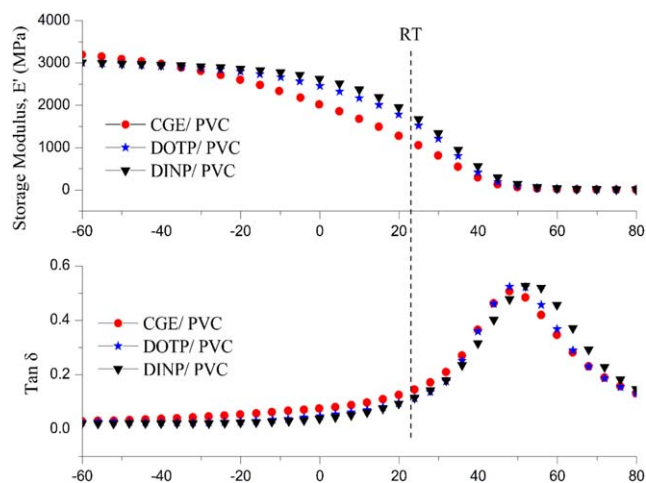


Figure 4. Dynamic mechanical analysis in storage modulus (E') and $\tan \delta$ for the PVC samples with different plasticizers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to the presence of cyclic C—O—C asymmetric and symmetric stretching vibrations, respectively. These variations indicate that the CD had reacted and formed ether group.

NMR is another important technique employed to investigate the structure of the synthesis product of CD. Figures 2 and 3 displayed the ^1H NMR and ^{13}C NMR of CD and CGE, respectively. In Figure 2, the peaks at 6.7–7.2 ppm corresponding to the protons on the benzene structure next to phenolic hydroxyl group. The appearance of the peak at 5.05 ppm corresponds to the proton of phenolic hydroxyl.³² The peak at 5.38 ppm represents the methine protons of —CH=CH— groups. And the peaks at 0.9–2.8 ppm correspond to the methyl, methylene, and methine protons on different alkyl chains of CD.³³ When comparing the spectrum of CD and CGE, the major difference between them is the glycidyl ether group. The chemical shifts of hydrogens at 2.86, 3.37, 3.98, 4.21, and 5.05 ppm clearly reveal the existence of glycidyl ether in Figure 2. The ^{13}C NMR chemical shifts at 110.59–129.90 ppm corresponding to double bonds were clearly demonstrated in Figure 3. The chemical shifts at 22.07–31.58 ppm represented methyl, methylene, and methine protons on alkyl chains. As shown, the glycidyl ether group made a distinction between CD and CGE. The chemical shift of the benzene ring carbon from 154.86 to 158.15 ppm shows the phenolic hydroxyl transferred into an ether when CD progressed into CGE.³⁴ The chemical shifts of the three carbons in the glycidyl ether group occurred at 44.05, 49.71, and 68.13 ppm, respectively.

DMA, Tensile Properties, and Hardness Character

The results of thermomechanical properties of the obtained PVC samples are depicted in Figure 4 and Table II. It is seen

Table II. Storage Modulus (E'), Glass Transition Temperature (T_g), 10% And 50% Weight Loss Temperatures (T_{10} And T_{50}) For Different Pvc Samples

Samples	E' at -50°C (MPa)	E' at -30°C (MPa)	E' at RT (23°C) (MPa)	T_g ($^\circ\text{C}$)	T_{10} ($^\circ\text{C}$)	T_{50} ($^\circ\text{C}$)
CGE/PVC	3092.58	2813.69	1135.91	48.36	280.39	326.69
DOTP/PVC	2970.12	2878.87	1635.31	49.73	257.70	300.20
DINP/PVC	2986.81	2921.51	1775.88	53.30	252.62	295.1

that the DOTP/PVC and DINP/PVC displayed a similar trend in which E' remains at a high level about 3000 MPa below -30°C , decreases sharply in a wide range from -30°C to 50°C , and is close to a constant level below 150 MPa above 50°C . Whereas the E' of CGE/PVC was slightly higher than that of both commercial plasticizers when below -40°C , and decreases slowly and continuously from -60°C to 50°C . The difference in thermomechanical performance of the samples was probably caused by the structural features of the plasticizer and can be explained through the following aspects. First, the CGE contains terminal epoxy group and ether group, which has higher space flexibility than ester groups in DOTP and DINP, and provides more opportunity for hydrogen bonding (Figure 5) by attracting PVC molecules and reducing steric hindrance effects.¹ Furthermore, as reported, the rigidity of a plasticized system depends on the hydrogen bonding present when the PVC matrix exhibited glassy state characteristics just before the random motion of the polymer chains was frozen.¹ So the CGE/PVC possessed higher E' value when below -40°C . Second, CGE had lower molecular weight than phthalates, which means the relative content of functional groups would be increased when at a similar plasticizer load. As a result, the plasticizing efficiency is probably improved. Third, CGE had longer alkyl chains, good lubricate, and created more free volume as the temperature increased. As shown in Figure 5, the motion increased the space between polymer molecules reducing polymer–polymer interactions at sites where polymer chains could associate, thereby decreased the value of E' above -60°C .

In addition, all samples exhibited a single T_g , indicating the three formulations formed homogeneous materials and a good miscibility of CGE with PVC.²⁶ As shown in Table II, CGE/PVC had a maximum decrease of 9.27% in T_g compared with those of DOTP/PVC and DINP/PVC, indicating a more efficient plasticization system. This result was also confirmed by $\tan \delta$ peak shifting toward lower temperatures and becoming broad.³⁵

Moreover, it can be observed from Figure 4 that at the RT, CGE/PVC has the maximum E' and minimum $\tan \delta$, corresponding to great softness and flexibility.³⁶

The changes in tensile strength, elongation at break, elastic modulus, and shore A hardness of the obtained plasticized PVC samples are shown in Figure 6. The tensile strength and elastic modulus values of different formulations followed the order of DOTP/PVC (35.15 MPa, 0.43 GPa) > DINP/PVC (32.35 MPa, 0.34 GPa) > CGE/PVC (24.63 MPa, 0.21 GPa). Compared with the former samples plasticized with phthalates, CGE/PVC demonstrates increases of 17.6% and 17.3% in elongation at break, respectively. Furthermore, Figure 6 indicates that the CGE/PVC showed lower 2.3% and 2.9% hardness than DOTP/PVC and

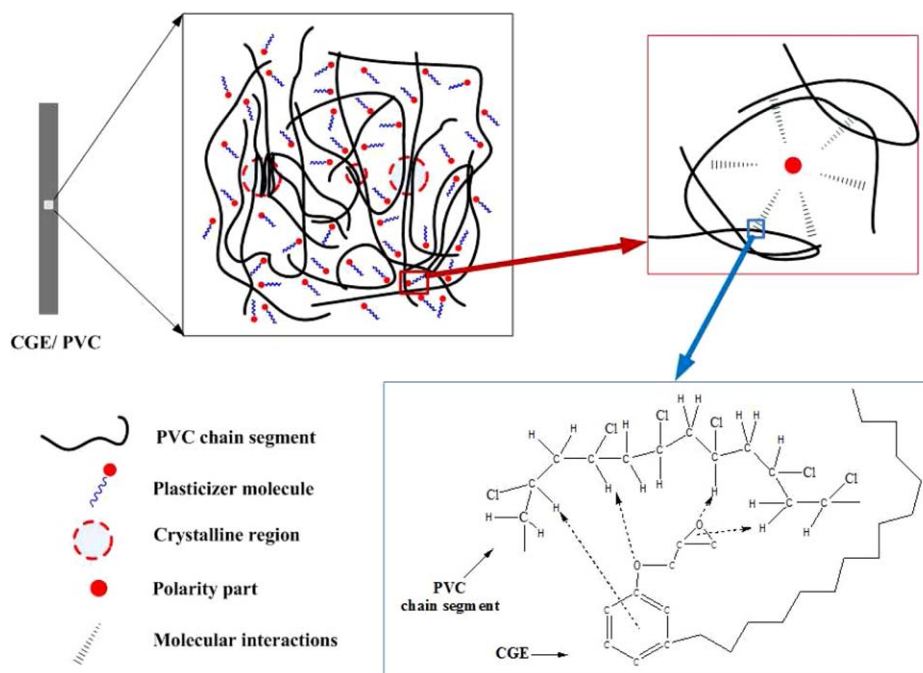


Figure 5. Possible interaction between CGE and PVC molecules in the plasticized system. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

DINP/PVC, respectively. These results are consistent with the DMA results, indicating that CGE has a significant effect on the flexibility properties and exhibits the best toughness. It can also be concluded that lower concentrations of CGE are required to reach the same flexibility than the higher concentrations needed for DOTP and DINP.

The results reported from Figures 4–6 can be explained according to the solubility parameter theory. The solubility parameters of PVC and plasticizer can be determined using the small eq. (1), which is more accurate for plasticizers in low molecular weight.³⁷

$$\delta = (\text{CED})^{1/2} = \left[\frac{\Delta E}{V_i} \right]^{1/2} = \frac{\sum F_i}{V_i} \quad (1)$$

$$= \frac{\rho \sum F_i}{M} = \frac{x_1 \sum F_1 + x_2 \sum F_2 + \dots + x_n \sum F_n}{x_1 V_1 + x_2 V_2 + \dots + x_n V_n}$$

where δ is the solubility parameter, V_i is molar volume, ΔE is energy of vaporization, and F_i is the molar attraction constant, M and ρ are the molecular weight and density of the plasticizer or chain unit of the polymer, respectively.

Furthermore, according to van Krevelen,³⁸ good solubility between plasticizers and polymer occurs when the difference in value of the solubility parameter [eq. (2)] is as small as possible:

$$DS = \delta_{\text{PVC}} - \delta_{\text{Plasticizer}} \quad (2)$$

where $\delta_{\text{Plasticizer}}$ and δ_{PVC} denote the solubility parameter of the plasticizer and polymer, respectively.

The values of different terms calculated according to eqs. (1) and (2) are reported in Table III. It can be seen that the DS of CGE is slightly lower than that of DOTP and DINP, indicating a good miscibility between CGE and PVC. So CGE shows higher ability to lubricate by incorporating itself among the

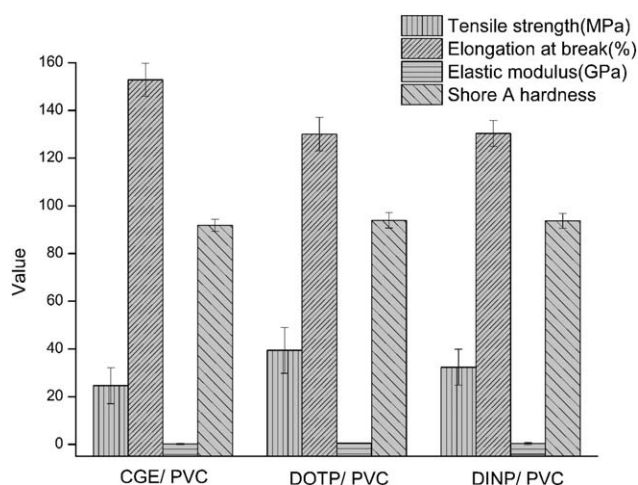


Figure 6. Tensile properties and hardness character of PVC samples with different plasticizers.

Table III. Solubility Parameters for Plasticizers and PVC

Items	δ (J/cm ³) ^{1/2}	DS (J/cm ³) ^{1/2}
PVC	9.66 ⁴⁶	-
DOTP	8.90	0.76
DINP	8.31	1.35
CGE	9.01	0.65

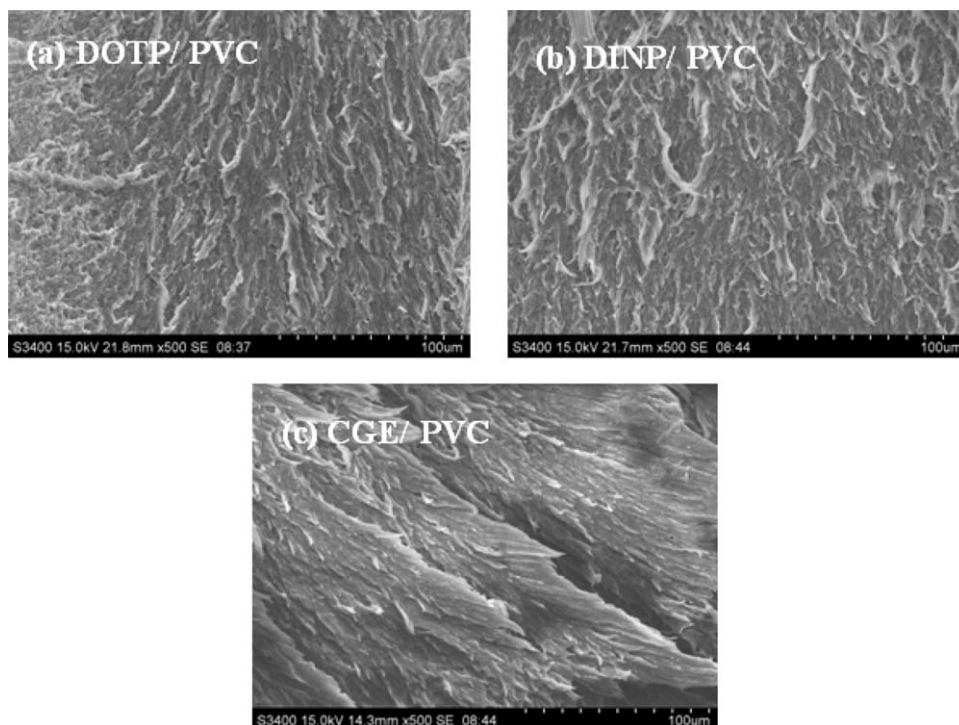


Figure 7. SEM microphotographs of fractured surface of PVC samples with different plasticizers.

polymer chains, reducing PVC–PVC interactions by replacing part of plasticizer–PVC interactions,¹ and increasing the free volume of the amorphous part of PVC.^{39,40} This explains why CGE shows good plasticizing effect than the other two commercial plasticizers.

Microstructure

The plasticizing effects can also be observed using SEM on fractured surfaces of the samples as obtained from the mechanical tests (Figure 7). Figure 7(a) corresponded to PVC plasticized by DOTP and a homogeneous matrix could be seen. Furthermore, some indicators of plastic deformation were visible since the

wave structure was formed.⁴¹ But there are still some individual PVC particles and aggregates on the fractured surfaces, which is responsible for the lower mechanical properties. This situation can also be observed in Figure 7(b). As shown in Figure 7(c), we can observe the formation of a homogeneous matrix and the plasticizer seemed to have solvated the PVC thoroughly. Furthermore, waves and threads can be seen in the fractured surface which leads to a remarkable increase in mechanical properties. The results are in agreement with the mechanical properties previously investigated.

Thermal Stability

The TG and DTG curves of PVC samples with different plasticizers are shown in Figure 8. It was observed from the DTG curves that all the samples are thermally stable in nitrogen gas below 200°C and mainly displayed two-stage thermal degradation above this temperature. In the first degradation (about 220–400°C), dehydrochlorination of PVC accelerates as well as crosslinking reaction of PVC on account of the formation of conjugated polyene sequences after dehydrochlorination.^{42,43} With the rise of temperature, the formed compounds resulting from crosslinking reaction began to degradation and decompose, which decreases the mass loss of PVC as well as the evolution of HCl.⁴⁴ The second stage (>450°C) was corresponding to the decomposition of the aromatic compounds formed by the cyclization of conjugated polyene sequences, producing short-chain alkanes or alkenes.^{43,45} Table II summarizes the thermal data of these obtained samples, including the temperature at which 10% and 50% weight loss occurs (T_{10} and T_{50}). It can be seen clearly that both temperatures increase to maximum values at CGE/PVC, which is due mainly to the glycidyl ether group of CGE can suck and react with the HCl, inhibit

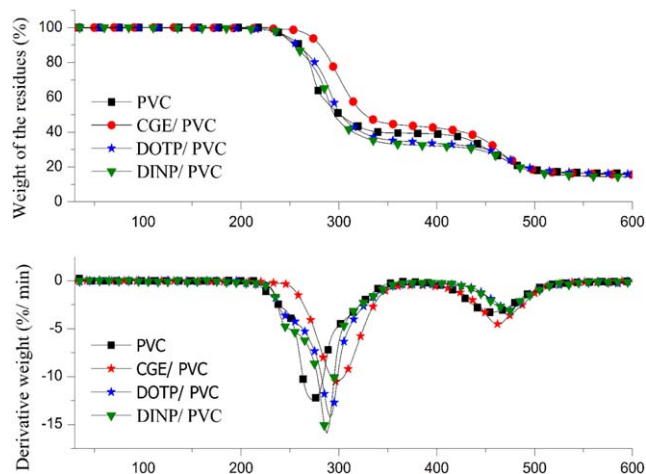












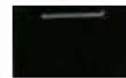










Figure 8. TG and DTG curves of the PVC samples with different plasticizers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Discoloration of PVC Samples With Different Plasticizers, Heated at 185°C

Formulations	0 min	10 min	20 min	30 min	40 min	50 min	60 min
CGE/ PVC							
DOTP/ PVC							
DINP/ PVC							

dehydrochlorination, and delay the degradation events.^{46–48} Compared with the pure PVC, DOTP/PVC, and DINP/ PVC, the CGE/PVC had maximum increase of 27.77°C and 31.59°C in T10 and T50, respectively. Hence, the CGE is more effective on improving the thermal stability of PVC than the commercial plasticizers DOTP and DINP.

Discoloration test at 185°C is employed to analyze the function of degradation times of the obtained PVC samples. As shown in Table IV, the PVC samples containing DOTP and DINP exhibited excellent early color retention within 30 min, but turned black almost completely within 40 min as a consequence of the thermal degradation of PVC resin.^{14,49,50} The evolution on the effect of CGE can also be clearly observed in Table IV. Due to the natural color of CGE, the CGE/PVC film displayed light yellow coloration. After heating for about 10 min, the color became a slightly deeper yellow and then resisted further observable change for 60 min. So by following the color changes, it is possible to estimate that the PVC sample plasticized with CGE has longer stability time compared with those

plasticized with phthalates. That may be because the glycidyl ether group of CGE can react with HCl generated by the degradation process and inhibit production of large amounts of polyene sequences in the polymer chains that may produce an undesirable color. As a result, the PVC sample plasticized by CGE exhibited the highest thermal stability and the lightest color after 30 min compared to those plasticized by DOTP and DINP.

Processability

Dynamic stability of obtained samples was tested by Haake torque rheometer to investigate the effects of plasticizers on the processability of PVC. Figure 9 shows the curves of dynamic thermal stability time of PVC samples at 180°C. The results of degradation time, balance torque and stability time are summarized in Table V. Compared with DOTP/PVC and DINP/PVC, the CGE/PVC has a maximum increase of 25.31 min in dynamic stability time and a maximum decrease of 1.2 Nm in balance torque. All of the results indicate CGE can improve the processability of PVC prominently by reducing the melt viscosity during processing and extending the processing time.¹ On the other hand, these results are consistent with the TGA results, also suggesting that CGE increased the stability time and the induction time of PVC.

Volatility and Exudation Properties

The weight losses of the PVC samples by volatility and exudation are shown in Figure 10. These properties of the plasticizers from the polymer were strongly dependent on the molecular weight, solubility, compatibility, and chemical structure of the plasticizers.⁵¹ It can be seen that the volatility loss decreased in the following order: CGE/PVC, DINP/PVC, and DOTP/PVC. It

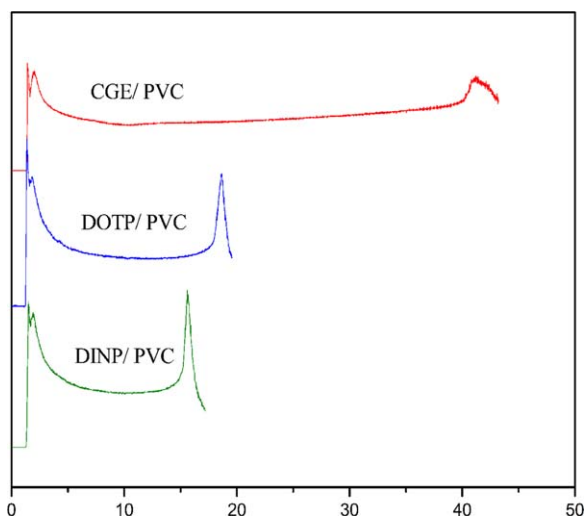


Figure 9. Effect of different plasticizers on dynamic thermal stability of PVC at 180°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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

Formulation	Dynamic stability time (min)	Balance torque (Nm)
CGE/PVC	35.96	5.8
DOTP PVC	12.78	6.0
DINP/PVC	10.65	7.0

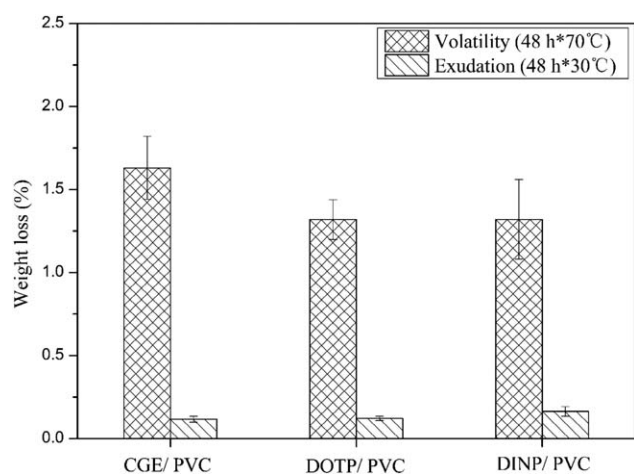


Figure 10. Weight losses of PVC samples after volatility and exudation tests.

was suggested that the volatilization loss was largely depended on the molecular weight of the plasticizer, so the CGE had the highest weight loss. As discussed above, DOTP had higher compatibility with PVC compared with DINP, so it has stronger interactions with PVC and lower weight loss.

As shown in Figure 10, the three samples presented similar exudation loss. And weight loss of DOTP/PVC was slightly higher than the other two. This result was according to the results of compatibility.

CONCLUSIONS

In this study, new natural plasticizer CGE was prepared by a two-step modification process and incorporated into semi-rigid PVC. The plasticizing performance of CGE was mainly evaluated by the analysis of DMA, mechanical properties, Small equation, SEM, TGA and dynamic stability analysis, and compared with those of the commercial plasticizers DOTP and DINP. DMA, mechanical properties, and SEM analysis suggested that CGE has the best compatibility and plasticizing effects on PVC. Furthermore, TGA and dynamic stability analysis tests shown the CGE/PVC system exhibited a highest thermal stability and a significantly processability. CGE also has slightly lower volatility resistance and higher exudation resistance than that of DOTP and DINP. Thus, due to its good mechanical compatibility, thermal properties, processability, and exudation resistance, CGE has the potential to alternatives of petroleum-based plasticizers in fully replacement in semi-rigid PVC. In addition, since it was produced from renewable, environmental friendly, biodegradable, and easily available raw materials, the natural plasticizer CGE will reduce the dependence on petroleum-based plasticizers.

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