

# Thermal degradation and plasticizing mechanism of poly(vinyl chloride) plasticized with a novel cardanol derived plasticizer

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**Abstract.** A natural plasticizer cardanol derivatives glycidyl ether (CGE) was synthesized and employed as a plasticizer for the poly(vinyl chloride). The effect of CGE on thermal degradation of PVC films and its plasticizing mechanism were firstly reported. The molecular structure of CGE was characterized with Fourier transform infrared spectroscopy (FTIR). Thermal properties, degradation properties and compatibility of the PVC films were investigated by Differential scanning calorimeter analysis (DSC), Thermogravimetric analysis (TGA) and FTIR, respectively. Compared with the commercial plasticizers dioctylphthalate (DOP), CGE can endow PVC film with a decrease of 4.31 °C in glass transition temperature ( $T_g$ ), an increase of 24.01 °C and 25.53 °C in 10% weight loss ( $T_{10}$ ) and 50% weight loss ( $T_{50}$ ) respectively, and a higher activation energy of thermal degradation ( $E_a$ ).

## 1. Introduction

Plasticizers have become the most consumable additive in PVC which can improve the mechanical properties, processability, and thermal stability of the poly(vinyl chloride) (PVC). Since their potentially toxic effects on human health and environmental impact [1-5], the use of phthalates is incontrovertibly becoming more limited. Hence, there is a trend to replace phthalates by alternative plasticizers [6-8]. Currently, there is growing interest in the research and use of natural-based plasticizers which are characterized by low toxicity [8-11]. They mainly include modified and epoxidized triglyceride oils from soybean oil, linseed oil, sunflower oil, glycerol monoester, and fatty acid esters [12-14]. As the plastics industry and environmental awareness continues to grow, there is an urgent and unmet need to develop new natural plasticizers with improved properties and cost competitiveness.

Cardanol is an extracted product from cashew nut shell liquid, which is one of the most commonly used renewable agricultural resource materials [15]. Due in part to its versatile chemical structure and low cost, cardanol can be considered to be a very promising raw-material to develop new derived materials to be used in environmentally friendly processes [16,17]. Cardanol and its derivatives usually have major applications in synthetic resins [18, 19] bio-composites [20], epoxy curing agents [21] and coatings [22-24]. Recently, cardanol with or without modification has been used as a plasticizer in the polymer and rubber industries, showing significant plasticizing effects [25, 26].



Furthermore, cardanol-based plasticizers have been reported to be a kind of efficient plasticizer for PVC [17, 27-29].

The present work provided a novel method to prepare cardanolglycidyl ether (CGE), and firstly reported the effect of CGE on thermal degradation of PVC films and its plasticizing mechanism. The thermal stability, degradation properties and compatibility of the plasticized PVC films were evaluated by the DSC, TGA and FTIR. The plasticizing effect of CGE was comparable to that of commercial phthalate ester plasticizer DOP. The objective of this work is to demonstrate that the heat resistant plasticizer derived from renewable resource cardanol can offer excellent thermal stability and compatibility for PVC and provide new idea for development of special bio-plasticizer.

## 2. Experimental

### 2.1. Materials

Cardanol (stabilized, 88.5%) was purchased from Shanghai Meidong Biological Material Co., Ltd., China. The refractive index ( $n_D^{25}$ ) of Cardanol is 1.509, viscosity is 46 mPa·s (25°C), density is 0.928 g/cm<sup>3</sup> (25°C). Cardanol was used after distillation. Epichlorohydrin, sodium hydroxide (98.7%), calcium oxide (98%), 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 Diisononyl phthalate (DINP) (99%) were obtained from Aladdin Chemical Reagent Co., Ltd., China, and were used as received.

### 2.2. Preparation of CGE

300 g Cardanol was charged into a flask equipped with a fractional distillation device. A pale yellow distillate was obtained within 240.0–260.0 °C under a high vacuum of 8 Torr. 100.0 g (0.332 mol) of cardanol, 245.0 g (2.64 mol) of epichlorohydrin and 1.8 g (0.0097 mol) benzyltriethyl ammonium chloride were introduced into a 250 ml flask equipped with mechanical stirrer, reflux condenser and thermometer. Then the mixture was slowly heated to 117 °C and kept reacting for 2.0 h. After the mixture was cooled to 60 °C, 13.3g (0.332 mol) sodium hydroxide was charged, and the reaction was continued at 60 °C for 3h. The excess epichlorophydrin was distilled to be recycled and the solids were filtered. 108.6g of a yellowish low-viscosity compound was obtained (yield: 91.01 % relative to Cardanol).

### 2.3. Preparation of plasticized PVC test specimens

A series of plasticized PVC specimens with different plasticizers at different concentrations were prepared. The compositions are shown in table 1. First, PVC powder (100 g), plasticizers (25g), and thermal stabilizers (2.0g, Ca soap/Zn soap = 3/1) were mixed using a mechanical mixer at room temperature (RT) for 5 min. Second, the mixture was compounded into a homogeneous mixture at 160 °C for 5 min by aPlasti-Corder Lab-Station (South Hackensack, NJ). Finally, the films were made using a Carver 3969 mini hot press (Wabash, IN) at 170 °C for 5 min.

**Table 1.** The composition of PVC blends.

Component	CGE/ PVC	DOP/ PVC
PVC (g)	100.00	100.00
CGE (g)	25.00	0.00
DOP (g)	0.00	25.00
Thermal stabilizer (g)	2.00	2.00

## 2.4. Characterizations

Fourier transform infrared (FTIR) analysis was conducted using a Nicolet IS10 spectrometer (Thermo Fisher Scientific Inc., USA) by an attenuated total reflectance method. The samples were scanned from 4000 to 500  $\text{cm}^{-1}$ .

Differential scanning calorimetry (DSC) analysis was performed on a Diamond instrument (Perkin-Elmer Co., USA). Each sample was scanned from -60 °C to 80 °C under a nitrogen atmosphere at a heating rate of 10 °C/min.

Tensile properties were measured using a SANS CMT-4303 universal testing machine (Shenzhen XinsansiJiliang 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.

Thermogravimetric analysis (TGA) was carried out in a thermogravimetric analyzer (NetzschCo., Germany). Each sample was scanned from ambient temperature to 400 or 600°C at a heating rate of 5, 10, 15, 20, and 25 °C/min, respectively. The TGA experiment was performed under a 60 mL/min nitrogen flow. The kinetic parameters such as activation energy ( $E_a$ , KJ/mol) and pre-exponential factor ( $A$ ) were evaluated by the Kissinger equation:

$$\ln\left(\frac{\beta}{T_{\max}^2}\right) = \ln\frac{AR}{E_a} - \frac{E_a}{R} \frac{1}{T_{\max}} \quad (1)$$

where  $R$  = Gas constant (8.314 J/mol•K). Equation (1) indicates that  $\ln(\beta/T_{\max}^2)$  and  $1/T_{\max}$  are in a linear correlation.  $E$  and  $A$  can be calculated from the slope ( $a$ ) and intercept ( $d$ ) on the curves of  $\ln(\beta/T_{\max}^2)$  change versus  $1/T_{\max}$ .

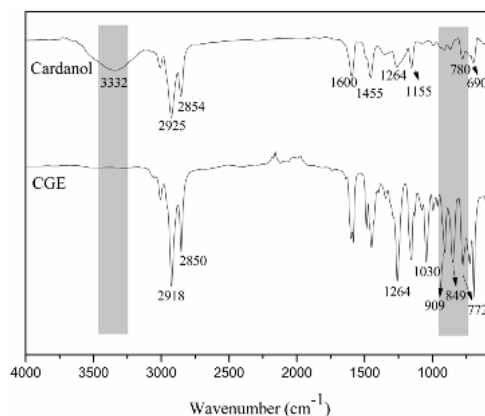
$$E_a = -a \bullet R \quad (2)$$

$$\ln(A) = d + \ln\left(\frac{E_a}{R}\right) \quad (3)$$

## 3. Results and discussion

### 3.1. Characterization

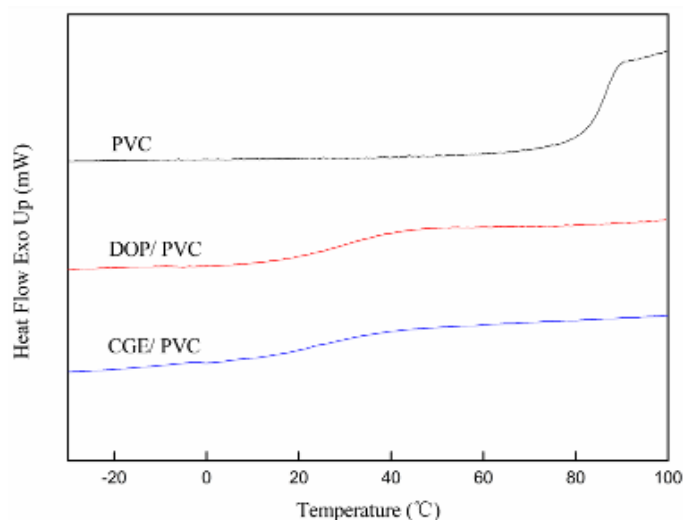
Figure 1 shows the FTIR spectra of cardanol and CGE. Compared with CGE, the FT-IR spectra of cardanol showed abroad band at around 3332 $\text{cm}^{-1}$ corresponding to phenolic hydroxyl group. The unsaturated alkyl chains at 3009  $\text{cm}^{-1}$ appeared in the FT-IR of cardanol. The broad band phenolic hydroxyl group disappeared in the spectra of CGE, and ether group were found at 772, 849 and 909 $\text{cm}^{-1}$ , which indicated that the epoxidation reaction occurred. Furthermore, new peaks appear at 1264 and 1030  $\text{m}^{-1}$  due to the presence of cyclic C—O—C asymmetric and symmetric stretching vibrations, respectively. All of theses data may suggest that the cardanol had reacted and formed ether group.



**Figure 1.** FT-IR spectra of cardanol and CGE.

### 3.2. DSC

Figure 2 compares the DSC thermograms of PVC films with and without plasticizers, the traces demonstrate a characteristic change in thermal properties assigned to a glass transition ( $T_g$ ). The pure PVC film had a  $T_g$  temperature of approximately 85.63 °C (table 2) whilst the DOP/ PVC and CGE/ PVC films have significantly lower  $T_g$  of 30.87 °C and 26.56 °C respectively. It can be seen that CGE/ PVC had a maximum decrease of 4.31 °C in  $T_g$  compared with that of DOP/ PVC, indicating a more efficient plastization system[17].



**Figure 2.** DSC curves of the PVC films.

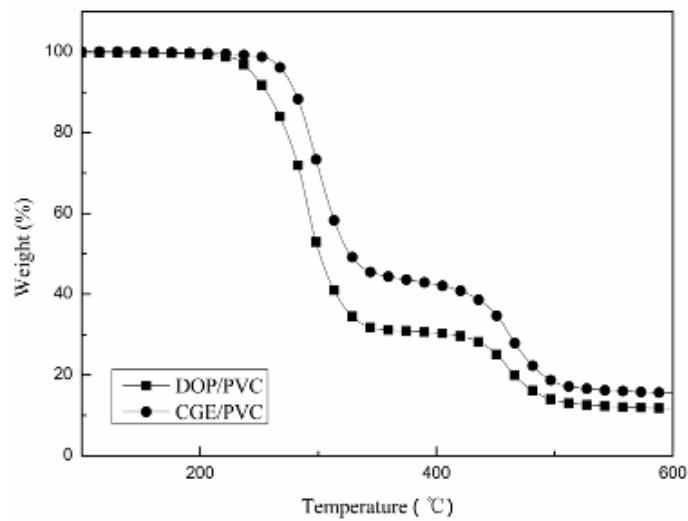
**Table 2.** Glass transition temperature ( $T_g$ ), 10% and 50% weight loss temperatures ( $T_{10}$  and  $T_{50}$ ) for different PVC samples.

Sample	$T_g$ (°C)	$T_{10}$ <sup>a</sup> (°C)	$T_{50}$ <sup>a</sup> (°C)	Carbon residue (%)
CGE/ PVC	26.56	280.39	326.69	15.54
DOP/ PVC	30.87	256.38	301.16	11.69

<sup>a</sup>Values of 10 °C/min.  $T_i$ : onset temperature of TGA.

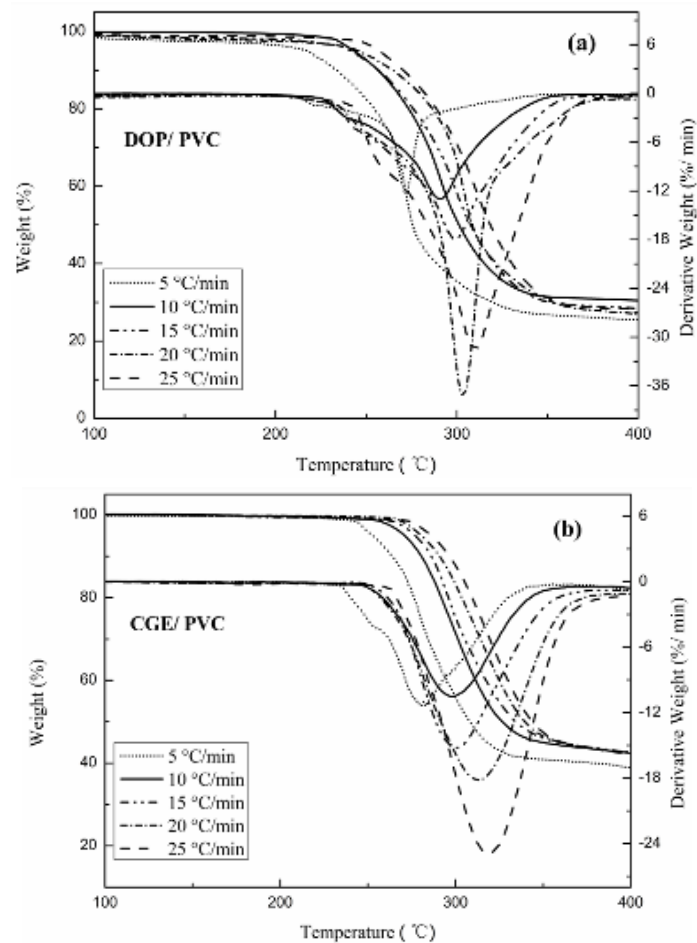
### 3.3. Thermal stability and degradation kinetics

Figure 3 shows the TGA curves of the films with different plasticizers heated in nitrogen at the rate of 10 °C/min. It can be observed that both of the samples are thermally stable in nitrogen gas below 200 °C and mainly displayed three-stage thermal degradation above this temperature. The first stage degradation (about 230-350 °C) is the fastest and corresponded to dechlorination of PVC, with formation and stoichiometric elimination of HCl and a few chlorinated hydrocarbons. [30] The formation of aromatic compounds by the cyclization of conjugated polyene[31, 32] mainly occurred in the second stage (about 350-420 °C). In the last stage (> 420 °C), the second degradation was shown, which is mainly contributed to the degradation of the complex structures resulting from aromatization.[33] Furthermore, the TGA characteristic temperatures of PVC films are illustrated in Table 2, including the 10% and 50% weight loss temperatures ( $T_{10}$  and  $T_{50}$ ), and carbon residue for the degradation. It clearly can be seen that CGE improves the thermal stability of PVC films. Compared with DOP/ PVC, the CGE/ PVC film had an increase of 24.01 °C and 25.53 °C in  $T_{10}$  and  $T_{50}$  respectively. As well as the carbon residue increased from 11.69% to 15.54%. This may be mainly due to the epoxy groups of CGE which can scavenge for HCl and delay the degradation events[34-36].

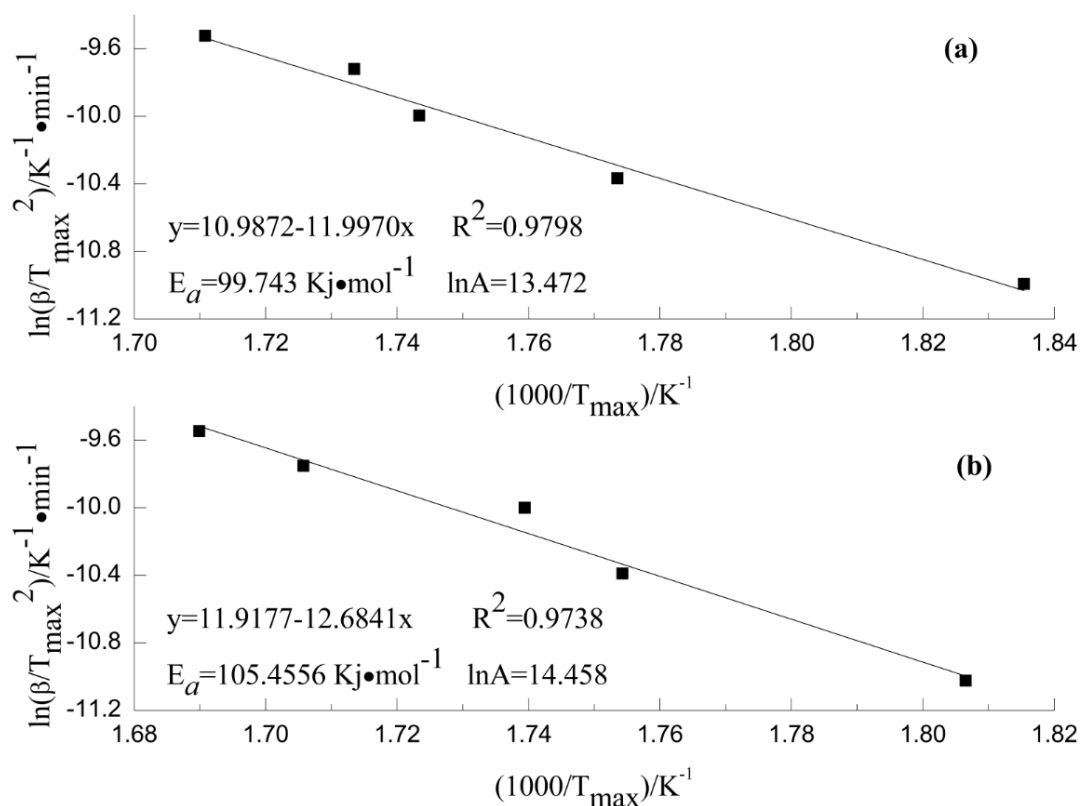


**Figure 3.** TGA curves of PVC films at a heating rate of 10 °C/min.

Figure 4 show the TGA and DTG thermograms of the PVC films heated in nitrogen at heating rates at 5, 10, 15, 20 and 25 °C/min. The kinetic parameters such as activation energy of thermal degradation ( $E_a$ , KJ/mol) and pre-exponential factor ( $A$ ) were evaluated by Kissinger equation. [37]



**Figure 4.** TGA and DTG curves at different heating rates of the (a) DOP/ PVC and (b) CGE/ PVC films.



**Figure 5.** Plots of  $\ln(\beta/T_{\max}^2)$  versus  $1000/T_{\max}$  and kinetic parameters for the PVC films (a) DOP/ PVC and (b) CGE/ PVC.

The kinetic parameters for the two plasticizers are summarized in figure 5. Compared with the DOP/ PVC, the CGE/ PVC had higher thermal degradation temperature. It was found that the  $E_a$  of GCE/ PVC ( $105.4556 \text{ KJ} \cdot \text{mol}^{-1}$ ) was higher than that of DOP/ PVC ( $99.7430 \text{ KJ} \cdot \text{mol}^{-1}$ ). Generally, a higher  $E_a$  suggests a higher thermal degradation resistance. The increase in the  $E_a$  could be explained by the enhancement of the intermolecular distance and chain mobility [38]. Hence, CGE could increase the thermal stability of the PVC matrix effectively.

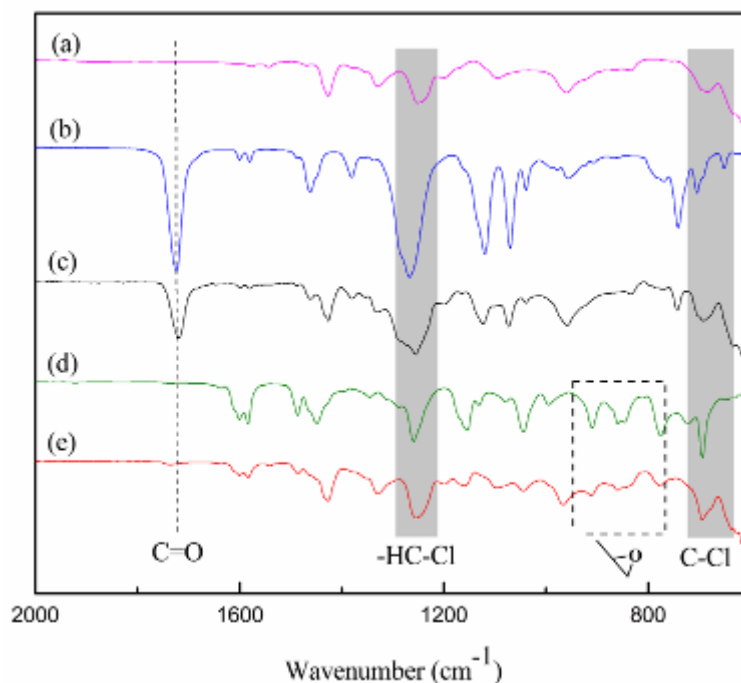
### 3.4. FT-IR

Figure 6 shows the FTIR spectra of pure PVC film, pure plasticizers, DOP/ PVC and CGE/ PVC films in the wavenumber range  $2000$  to  $600 \text{ cm}^{-1}$ . FTIR would be sensitive in situation where complexation has occurred in amorphous phase.[39] In the PVC films there are some characteristic peaks:  $\text{CH}_2\text{-Cl}$  angular deformation at  $1426 \text{ cm}^{-1}$ ,  $\text{CH-Cl}$  out of plane angular deformation at  $1254 \text{ cm}^{-1}$ ,  $\text{C-H}$  out of plane trans deformation at  $960 \text{ cm}^{-1}$ , and  $\text{C-Cl}$  bond stretching at  $831$ ,  $691$ , and  $615 \text{ cm}^{-1}$ . These characteristic bonds are in accordance with data found in the literature for PVC films.[36] After the incorporation of plasticizers into the formulations, the  $1724 \text{ cm}^{-1}$  band of  $\text{C=O}$  groups in DOP shifted about  $4\text{-}5 \text{ cm}^{-1}$  toward the lower frequency and its width increases. Furthermore, the glycidylether group in CGE shifted from  $910$ ,  $859$ ,  $847 \text{ cm}^{-1}$  to  $908$ ,  $858$ ,  $834 \text{ cm}^{-1}$ . This phenomenon can be mainly explained by equation (4) derived from Hooke's Law:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad (4)$$

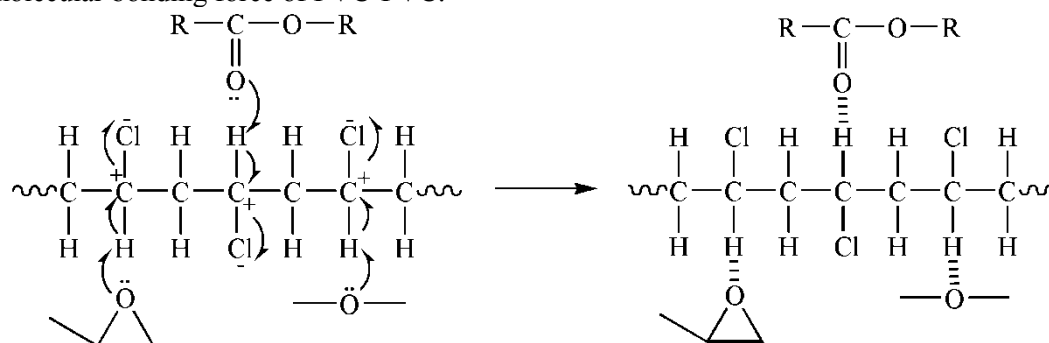
Where  $\nu$  is the vibration frequency,  $k$  is the force constant, and  $m$  is the mass. Eq. (4) shows the relationship of force constant to the wavenumber (vibration frequency). As the wavenumber decreases,

the force constant decreased, indicating the electronic was given by carbonyl group or epoxide groups, and formed hydrogen bonds with the hydrogen atom in PVC (as shown in figure 5). In addition, the shift of CH-Cl and C-Cl groups absorption frequencies of PVC shifted to frequencies several wave number higher (higher energy), indicating the introducing electron of the groups.



**Figure 6.** FTIR spectra of PVC films with different plasticizers: (a) pure PVC, (b) DOP plasticizer, (c) DOP/ PVC, (d) CGE plasticizer, and (e) CGE/ PVC.

This result is consistent with the proposed plasticization mechanism shown in figure 7. Besides that, it can be observed that the bands shift of CGE/ PVC was clearly than that of DOP/ PVC, showing stronger interaction between the polar parts of CGE (glycidylether group) and the PVC (carbon-chloride bond), the results has showed that the PVC plastization is the process of formatting the hydrogen-bonds between the carbonyl of the plasticizer and the hydrogen of PVC and weaker intermolecular bonding force of PVC-PVC.



**Figure 7.** Possible interaction between plasticizers and PVC molecular in the plasticized system.

#### 4. Conclusions

In summary, the CGE derived from cardanol has been evidenced as a high- performance plasticizer for improving thermal stability and degradation properties of PVC resin. Furthermore, DSC and FTIR analysis suggested that CGE has higher plasticizing effect and good compatibility on PVC compared



with the commercial plasticizer DOP. The results indicate that CGE could be a new bio-based plasticizer which can endow the PVC with higher thermal properties, lower cost and more eco-friendly.

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