

Synthesis, Characterization, and Application of a Bio-Based Plasticizer for PVC: Epoxidized Acetylation Cardanol

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ABSTRACT: A bio-based plasticizer, epoxidized acetylation cardanol, was synthesized from cardanol, which experienced acetylation reaction and epoxidation reaction. Chemical structure of epoxidized acetylation cardanol was characterized by FT-IR and ¹H NMR. Plasticized PVC films (PVC-P) were prepared by casting method with 40%wt of epoxidized acetylation cardanol as plasticizer. Thermal stability and plasticizing effect of PVC and PVC-P were investigated. The results presented that epoxidized acetylation cardanol enhanced the thermal stability of PVC-P and decreased glass transition temperature (T_g) from 81.9°C to 1.6°C. The tensile strength decreased from 26.60 MPa to 8.06 MPa, the elongation at break increased from 167.21 % to 905.44%. All of the results indicated that epoxidized acetylation cardanol could be used as main plasticizer for preparing flexible PVC materials.

KEYWORDS: Plasticizer; PVC; Cardanol; Synthesis; DSC.

INTRODUCTION

The plasticizer is an important plastic additive, which has been used widely in PVC products such as food packing, children toys, wire and cable, automobile tire, and building materials [1-2]. Phthalate plasticizers account 80% in all types of plasticizers around the world due to efficient plasticizing effect, low price and developed technology. However, phthalate plasticizers are easy to leach from PVC products to surroundings and human body, which will change properties of PVC products and decrease the service life. In addition, the potential reproductive toxicity of phthalate plasticizers prevents them using in children toys, food packing, medical

measurements and so on [3-5]. On the other hand, almost all of these phthalate plasticizers derive from petrochemical resources. With the increasing price of chemical products and depletion of petrochemical resources, the petrochemical resources-based chemical industry is unsustainable. In order to resolve the problem, bio-based plasticizers have been paid more attention [6-9].

Cardanol is a natural biomass phenol which derives from squeezing of cashew nut shell. The chemical structure of cardanol includes ring structure, hydroxyl groups and long chains, which is similar to that of phthalate plasticizers. The special chemical structure

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makes it possible to prepare different chemical products such as a plasticizer. In the present study, we synthesized a bio-based plasticizer: epoxidized acetylation cardanol. The preparing process included esterification and epoxy. The chemical structure of epoxidized acetylation cardanol was characterized by FT-IR and ^1H NMR. PVC plasticized with epoxidized acetylation cardanol was prepared using casting method and THF was used as solvent. Thermal stability and plasticizing effect of epoxidized acetylation cardanol on PVC were investigated. The study will provide a route for efficient use of cardanol. In addition, it will be a choice for replacing phthalate plasticizers used in PVC products.

EXPERIMENTAL SECTION

Materials

Cardanol (99%, acid value 5.5-6.6. Iodine value 210-250) was provided by Jining Hengtai Chemical Co., Ltd. Acetic anhydride, hydrogen peroxide solution (30%), formic acid, acetic anhydride, potassium carbonate, tetrahydrofuran(THF) was kindly provided by Nanjing Chemical Reagent Co., Ltd. Polyvinyl chloride (PVC) was supplied by Hanwha (South Korea).

Synthesis of acetylation cardanol

Cardanol and acetic anhydride with a molar ratio of 1:1.2 with potassium carbonate (1%wt) was settled in a 500 mL flask and stirring at 170°C for 3h to finish the reaction. Then the mixture was washed with deionized water until PH=7. The product was obtained after removing water(Yield 98.6%).

Synthesis of epoxidized acetylation cardanol

acetylation cardanol (30g) and formic acid (4.6g) was mixed in a 250mL flask and stirred at 65°C, then hydrogen peroxide(30%) solution (18g) was dropped in the mixture in 20min. The mixture was stirred at 65°C for 4h to finish the reaction. The product was washed with deionized water and obtained after removing water by evaporating under vacuum (Yield 96.4%, Epoxy value 4.20%). The Synthesis of epoxidized acetylation cardanol was presented in Fig. 1.

Sample preparation

PVC plasticized with epoxidized acetylation cardanol (PVC-P) was prepared with 20g of PVC resin and 8g of

epoxidized acetylation cardanol dissolving in 250mL of THF. The mixture was thoroughly agitated for 1 h at 60 °C until the mixture presented clear and transparent. The samples were then casted into Petri dishes (diameter 15 cm) and dried at ambient temperature for a week to remove traces of residual solvent and to obtain thin films. PVC sample without plasticizer was prepared using the same method[10-11].

Characterization

FT-IR studies were carried out using a Nicolet iS10 FT IR (Nicolet Instrument Corp., America). The spectra were acquired in the range of 4000 to 650 cm^{-1} at a resolution of 4 cm^{-1} .

^1H NMR measurements were conducted on an AV-300 NMR spectrometer (Bruker Instrument Corp., Germany) at a frequency of 400 MHz with CDCl_3 as solvent and tetrametylsilane (TMS) as an internal standard.

TGA was carried out in a TG 209F1 TGA thermal analysis instruments (Netzsch Instrument Corp., Germany) in N_2 atmosphere (50ml/min) at a heating rate of 10°C/min. The samples were put into platinum pans and scanned from ambient temperature to 600°C.

DSC was performed by a Diamond DSC differential scanning calorimeter (PE Instrument Corp., America). Slices of PVC materials with a total of 6mg were weighted and sealed in aluminum pans. The temperature of pans is from -60°C to 120°C at a heating rate of 10°C/min under a flow of nitrogen.

Tensile modulus, tensile strength, and elongation at break were determined according to GB/T 1040.1-2006 (China) under ambient conditions, using E43.104 Universal Testing Machine (MTS Instrument Corp., China).

RESULTS AND DISCUSSION

Chemical structure of products was characterized by FT-IR. Fig. 2 shows the FT-IR spectra of cardanol, acetylation cardanol, and epoxidized acetylation cardanol. Every characteristic absorption peak and wave number was labeled in Fig. 2. As seen from the FT-IR spectra of cardanol, the peak of hydroxyl absorption was at 3332 cm^{-1} , the peak at around 3009 cm^{-1} was attributed to olefin groups, methyl and methylene groups absorption peak was found at 2923 and 2852 cm^{-1} [12-13].

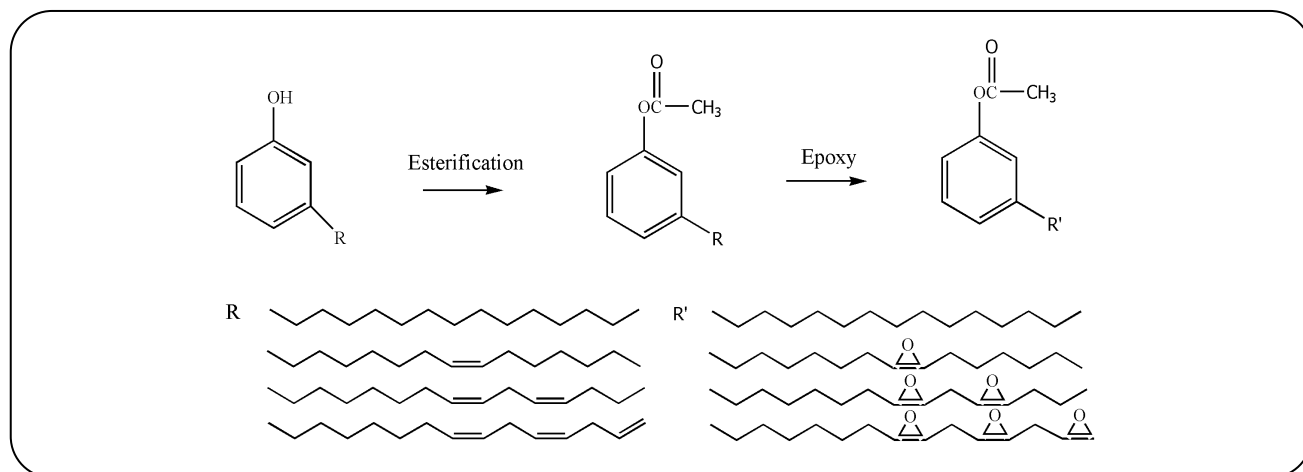


Fig. 1: Synthesis of epoxidized acetylation cardanol.

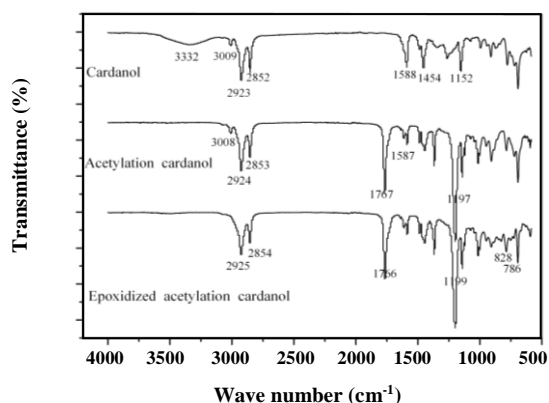


Fig. 2: FT-IR spectra of epoxidized acetylation cardanol.

After acetylation reaction, there was not any peak appearing at around 3332cm^{-1} , but a strong peak appeared at 1767 cm^{-1} corresponded to ester characteristic absorption peak, which indicated that acetylation reaction occurred. In the FT-IR spectra of epoxidized acetylation cardanol, the characteristic absorption peak of olefin groups could not be found at around 3008cm^{-1} , the C-O-C absorption peak was found at 786 and 828cm^{-1} [12-13]. The results illustrated that epoxidized acetylation cardanol was gotten.

The chemical structure of products was further investigated, ^1H NMR spectra of all products were detected. ^1H NMR spectrum of cardanol, acetylation cardanol, and epoxidized acetylation cardanol is showed in Figs. 3, 4 and 5, respectively. As seen from Fig. 3, the peak at 0.95 ppm corresponds to the terminal methyl protons of fatty acids ($-\text{CH}_3-$), the strong peak at 1.36 ppm , 1.41 ppm , 2.01 ppm ,

2.59 ppm , and 2.85 ppm corresponds to the methylene protons of fatty acids ($-\text{CH}_2-$) [12-15]. The ownership of every peak was labeled in Fig. 3. In addition, the peak for protons of $-\text{OH}$ was at $5.0-5.2\text{ ppm}$, the strong peak at 5.45 ppm was assigned to protons of olefin groups. The signals appeared at $6.3-7.4\text{ ppm}$ corresponds to the protons of benzene ring [16]. Compared to the ^1H NMR spectrum of cardanol, the peaks correspond to the protons of $-\text{OH}$ at around $5.0-5.2\text{ ppm}$ obviously presents weak in Fig. 4, and a strong peak at 2.30 ppm corresponds to methyl protons connected to ester groups [17]. All of these results indicated that acetylation reaction occurred but not finished completely, because there are some weak peaks in ^1H NMR spectrum of cardanol. Compared to the ^1H NMR spectrum of epoxidized acetylation cardanol (Fig. 5), the strong peak at 5.45 ppm was assigned to protons of olefin groups in Fig. 4 but cannot be found in Fig. 5, a new peak (peak 9 in Fig. 5) appeared at $\delta = 3.15\text{ ppm}$ which was assigned to protons on the epoxy groups, which indicated that the $-\text{CH}=\text{CH}-$ of acetylation cardanol was reacted with hydrogen peroxide solution. In addition, some insaturation residues were detected in the $6-5\text{ ppm}$ region, the amount of the residues was calculated using area normalization method. The results showed that the number of residues was only 0.3% of the total test sample based on the area normalization method. All of the results indicated that epoxidized acetylation cardanol was prepared.

Thermal stability of PVC and PVC-P was characterized with TGA measurements. Fig. 6 shows the TGA curves.

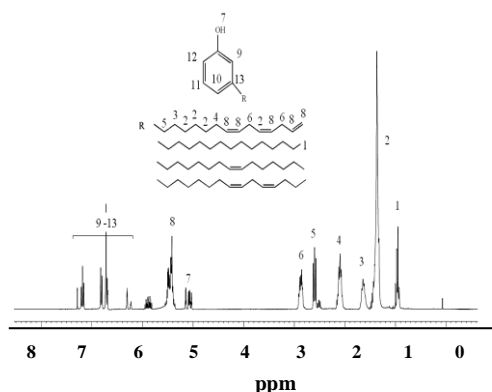


Fig. 3: ^1H NMR spectrum of cardanol.

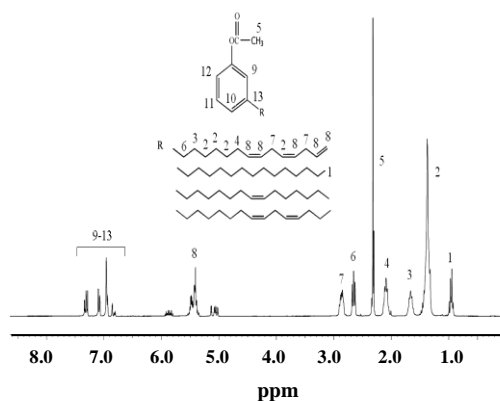


Fig. 4: ^1H NMR spectrum of acetylation cardanol.

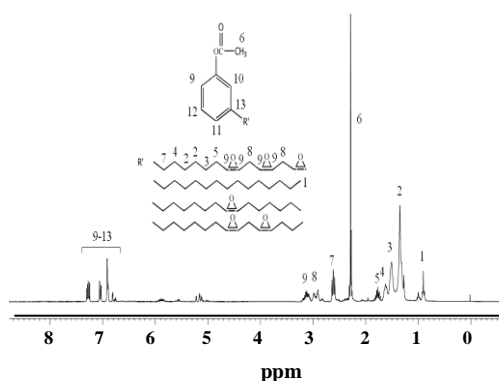


Fig. 5: ^1H NMR spectrum of epoxidized acetylation cardanol.

As seen in Fig. 6, the TGA curves of PVC and PVC-P exhibited two stages in the whole thermal degradation process. The first stage occurred at around 160°C and 320°C, which corresponds to the dehydrochlorination [18-19], and the decomposition of epoxidized acetylation cardanol. The second stage began 320°C and finished at 600°C, which was attributed to cyclization of conjugated polyene sequences to form aromatic compounds [20]. Obviously, TGA curve of PVC-P was delayed than that of PVC in the whole thermal degradation, which indicated that PVC-P was harder to decompose than PVC. Thermal stability of PVC-P was better than that of PVC. The reason can be explained with that benzene ring structure and ester groups of epoxidized acetylation cardanol was with high thermal stability[15], which further enhanced the thermal stability of PVC-P.

In order to investigate the plasticizing effect of epoxidized acetylation cardanol on PVC material, glass transition temperature (T_g) of PVC and PVC-P was characterized by DSC measurement. Fig. 7 presents the DSC curves of PVC and PVC-P. As seen from Fig. 7, PVC without plasticizer showed a high T_g of 81.9°C. T_g of PVC-P decreased from 81.9°C to 1.6°C with the addition of epoxidized acetylation cardanol. The addition of epoxidized acetylation cardanol in PVC matrix increased the distance of PVC chains and decreased the free volume then increased the motion of PVC chains, which finally made the PVC easily to process and apply [21-23]. Compared to the previous study, PVC plasticized with the same percentage composition of chlorinated phosphate based on soybean oil/DOP compound plasticizer or castor oil based polyol ester plasticizers /DOP compound plasticizer showed higher T_g and lower elongation at break than than epoxidized acetylation cardanol. The results indicated that the plasticizing effect of epoxidized acetylation cardanol on PVC was higher than chlorinated phosphate based on soybean oil and castor oil based polyol ester plasticizers [24-25]. All of these results illustrated that epoxidized acetylation cardanol was an efficient bio-based plasticizer.

Tensile test

Plasticizing effect of epoxidized acetylation cardanol was evaluated with tensile strength, elongation at break and modulus of elasticity. Table 3 shows the tensile

Table 1: Tensile properties of PVC and PVC-P.

Sample	Tensile strength (MPa)	Elongation at break (%)	Modulus of elasticity (MPa)
PVC	26.60	167.21	197.11
PVC-P	8.06	905.44	46.93

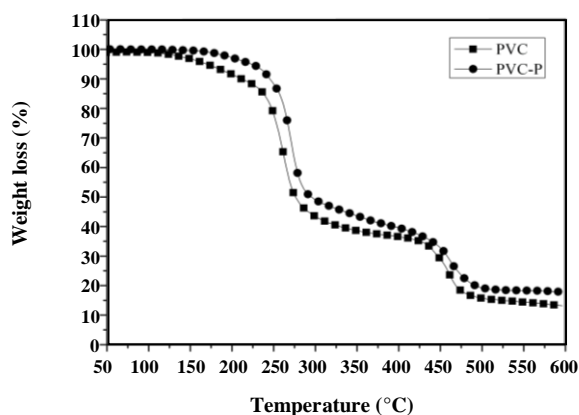


Fig. 6: TGA curves of PVC and PVC-P.

strength, elongation at break and modulus of elasticity of all PVC materials. PVC presented high tensile strength of 26.60 MPa and lower elongation at break of 167.21 %. The addition of epoxidized acetylation cardanol into PVC blends caused a significant decrease in tensile strength of 8.06 MPa and an increase in elongation at break of 905.44%, respectively. These data indicated that plasticizing effort of epoxidized acetylation cardanol was effective and could be used as main plasticizer for preparing flexible PVC materials.

CONCLUSIONS

In this study, we prepared a bio-based plasticizer (epoxidized acetylation cardanol) from cardanol experiencing acetylation reaction and epoxidation reaction. Chemical structure of epoxidized acetylation cardanol was characterized by FT-IR and ^1H NMR. Plasticized PVC film (PVC-P) was prepared using casting method with 40%wt of epoxidized acetylation cardanol as plasticizer. Properties of PVC and PVC-P were studied. The results presented that epoxidized acetylation cardanol improved the thermal stability of PVC-P and decreased glass transition temperature (T_g) from 81.9 °C to 1.6 °C. The tensile strength decreased from 26.60 MPa to 8.06 MPa, the elongation at break increased from 167.21 % to 905.44%. All of the results indicated that epoxidized acetylation cardanol could be used as main plasticizer for preparing flexible PVC materials. This study provided a route for efficient application of cardanol.

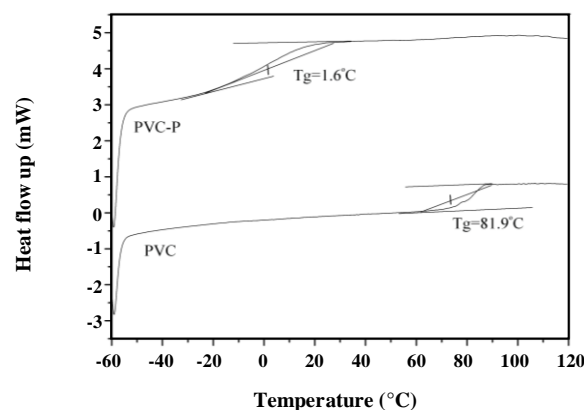


Fig. 7: DSC curves of PVC and PVC-P.

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