

Synthesis and Application of Environmental Castor Oil Based Polyol Ester Plasticizers for Poly(vinyl chloride)

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ABSTRACT: The use of vegetable oil based plasticizers can create new application for plasticized poly(vinyl chloride) (PVC) materials. In this study, novel environmental castor oil based polyol esters (COPE-1, ECOPE-1, COPE-2 and ECOPE-2) were synthesized and characterized with FT-IR and ¹H NMR. PVC materials were prepared via blending the synthesized castor oil based polyol esters as the main plasticizer. Properties of the PVC materials were investigated and compared to those of commercial plasticizers (DOP and ESO). The results showed that castor oil based polyol esters could significantly improve thermal stability of PVC blends. Plasticizing effect of COPE-2 and ECOPE-2 on PVC was better than that of DOP, ESO, COPE-1 and ECOPE-1. Migration stability and volatility stability of tests showed that with the increasing of the molecular weight of castor oil based polyol esters, the migration stability and volatility stability are enhanced. They could be with potential application used in food packing, children toys and medical devices as the main plasticizer.

KEYWORDS: Poly(vinyl chloride), Plasticizer, Castor oil, Migration



INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the synthetic materials in the five general synthetic resin (polyethylene, polypropylene, PVC, polystyrene and acrylonitrile butadiene styrene). PVC possesses a unique combination of physical and mechanical properties. The production volume of PVC is the second after polyethylene in the world. PVC can be used in the production of building materials, packing materials, electronic materials and goods for everyday consumption, which is widely used in these fields of industry, agriculture, transportation, electric power telecommunication and packing. These PVC products contain a large amount of plasticizers that could modify their thermal, mechanical and flame-retardant properties. At present, more than 500 kinds of plasticizers have been commercialized. The main commercial plasticizers are dioctyl phthalate (DOP) and dibutyl phthalate (DBP). 90% of plasticizers used in China are phthalate plasticizers. But these phthalates diffuse to surrounding easily and reduce performance of PVC products.¹ The low mass compounds of these phthalate plasticizers are found in domestic foods and wastes, and in animals and humans.^{2,3} Also, the loss of plasticizer caused changes in the long-time properties of the PVC products as well as possible toxic and biological effect when the plasticizers are transferred to humans.⁴ In addition, almost all of the phthalate plasticizers are derived from petroleum resources. With the gradual depletion of petroleum resources and rise of petroleum oil prices, chemical products from renewable resources have received much attention during the past decade. The use of vegetable oil as an alternative to petroleum based raw materials

to prepare chemical products constitutes a major contemporary challenge in terms of both economical and environmental aspects.^{5,6} Vegetable oils are preferred by the chemical industry due to their worldwide availability and relatively low prices. The main chemical structure of vegetable oils is triacylglycerols; the main components of triglyceride are saturated and unsaturated fatty acids, which could be used as platform chemicals for the synthesis of many polymers and monomers. Chemical products based on vegetable oil have been experienced fast development. Recently, we explored the synthesis and potential application of plasticizer from vegetable oil for PVC such as flame-retardant plasticizer based on castor oil (FRC),⁷ soybean oil phosphate ester (SOPE),⁸ flame-retardant plasticizer based on castor oil (PPC)⁹ and flame-retardant chlorinated phosphate ester based on castor oil (CPECO).¹⁰ All of these flame-retardant plasticizers could improve the thermal stability and flame-retardant performance of PVC blends. But the potential toxicity of phosphate structure restricts them using in food packing, children toys and medical materials. Hence, the environmental, biodegradable and low toxically epoxidized vegetable oil based plasticizers were paid more attention. Many researchers have prepared different environmental friendly plasticizers such as epoxidized safflower oil,^{11,12} epoxidized neem oil,¹³ epoxidized linseed oil,¹⁴ rice fatty acid polyester plasticizer¹⁵ and epoxidized soybean oil (ESO).^{16,17} These new plasticizers

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Table 1. Physical Properties of Products

	hydroxyl value (mg KOH/g)	acid value (mg KOH/g)	epoxy value (%)	viscosity (mPa·s 25 °C)	moisture content (%)
COP-1	420	0.82		1134	0.06
COP-2	478	0.72		2880	0.07
COPE-1		0.32		1470	0.10
COPE-2		0.36		3210	0.12
ECOPE-1		0.42	1.8	1960	0.14
ECOPE-2		0.41	1.4	2690	0.16

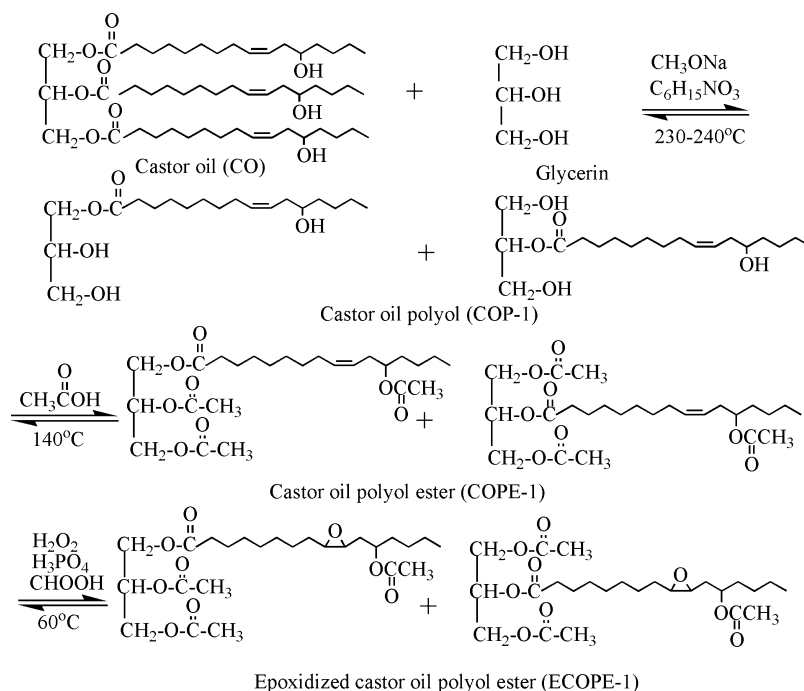


Figure 1. Synthesis of ECOPE-1.

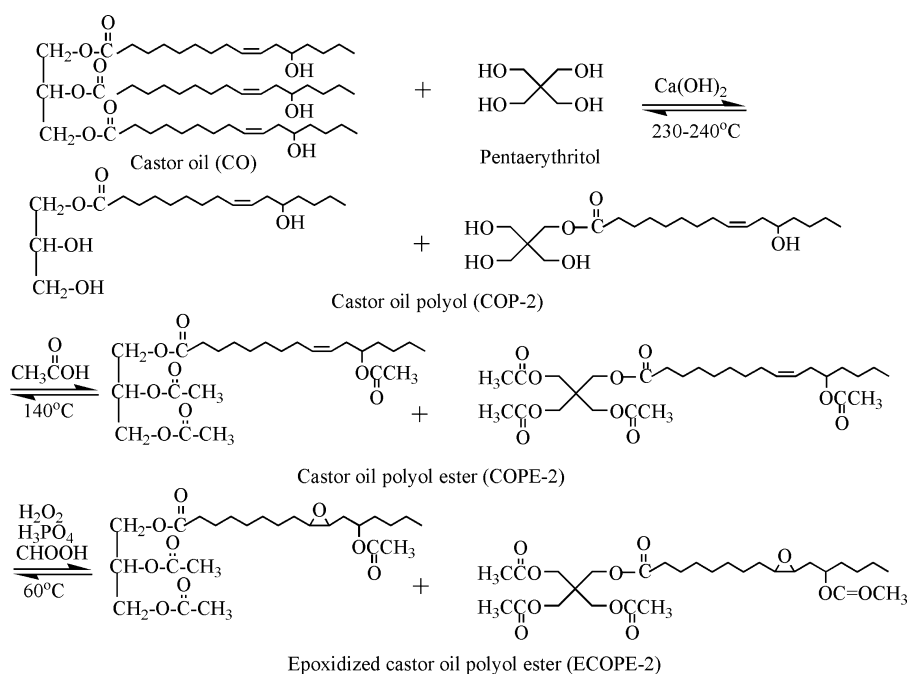


Figure 2. Synthesis of ECOPE-2.

derived from renewable resources that are environmental friendly plasticizers. However, there are a few double bonds in

the chemical structures of epoxidized vegetable oils, which reduces the compatibility with PVC. The poor compatibility

caused the plasticizer to migrate from the polymer matrix easily. The loss of plasticizer causes changes in mechanical, thermal and flame-retardant properties and electrical conductivity of the PVC products as well as possible toxic and biological effects when the plasticizers are transferred to humans. In general, the content of epoxidized vegetable oil used in flexible PVC products is 5%–10% of all plasticizers, only used as secondary plasticizers.¹⁸

In this study, we synthesized a series of polyol ester plasticizers from castor oil. The chemical structure of castor oil based polyol ester plasticizer was characterized with ¹H NMR and FT-IR. They are used as the main plasticizer for PVC. The plasticizing effect of these plasticizers on mechanical and thermal properties and migration resistance of PVC blends were investigated and compared to those of ESO and DOP.

■ EXPERIMENTAL SECTION

Materials. Pentaerythritol, glycerol, castor oil, phosphate, formic acid, 30% hydrogen peroxide solution, acetic anhydride, sodium hydroxide, DOP and ESO were provided by Nanjing Chemical Reagent Co., Ltd.(China). Polyvinyl chloride (PVC) was supplied by Hanwha (South Korea) with a *K* value of 65.0 and degree of polymerization of 1300 ± 100.

Synthesis of Castor Oil Polyol (COP-1). A four-necked round-bottomed flask equipped with a mechanical stirrer, condenser pipe, thermometer and provision for nitrogen flushing was charged with castor oil (250 g), sodium methoxide (0.09 g) and triethanolamine (1.8 g). The temperature was raised to 230–240 °C after continuous nitrogen for 20 min. Then 61 g of glycerol was placed into the mixture. The temperature was maintained at 230–240 °C.^{19–22} The acid value of the COP was detected at different reaction time. The reaction was stopped when the acid value of the reactants was less than 1.5 mg KOH/g. Table 1 shows the physical properties of all synthesized products. Figures 1 and 2 display the synthesis routes of all products.

Synthesis of Castor Oil Polyol Ester (COPE-1). 50 g of COP-1 and 50 g of acetic anhydride were mixed in a three-necked round-bottomed flask that was equipped with a mechanical stirrer, condenser pipe and thermometer. Then the mixture was stirred at 140 °C for 1 h to finish esterification. Then the reaction mixture was washed to pH = 7 with distilled water, and the water was removed with a rotary evaporator at 60 °C.

Synthesis of Epoxidized Castor Oil Polyol Ester (ECOPE-1). 100 g of COPE-1, 7.75 g of formic acid and 0.25 g of phosphoric acid were mixed in a four-necked round-bottomed flask that was equipped with a mechanical stirrer, condenser pipe, thermometer and constant pressure funnel. 80 mL of hydrogen peroxide solution was dropped in the reaction in 30 min and stirred at 60 °C for 8 h to finish epoxidation reaction. Then the reaction mixture was separated from water with a separating funnel and washed to pH = 7 with distilled water. Then the water was removed with a rotary evaporator at 60 °C.

Synthesis of Castor Oil Polyol (COP-2). 100 g of castor oil, 30 g of pentaerythritol and 0.65 g of calcium hydroxide were placed together in a 500 mL four-necked round-bottomed flask equipped with a mechanical stirrer, condenser pipe, thermometer and provision for nitrogen flushing. The reaction mixture was heat to 230 °C.^{20,22} The acid value of the COP was detected at different reaction time. When the acid value of the reactants was less than 1.5 mg KOH/g, the castor oil polyol was obtained.

Synthesis of Castor Oil Polyol Ester (COPE-2). 50 g of COP-2 and 66 g of acetic anhydride was mixed in a three-necked round-bottomed flask that was equipped with a mechanical stirrer, condenser pipe and thermometer, followed by stirring at 140 °C for 1 h to finish the esterification. Then the reaction mixture was washed to pH = 7 with distilled water and removed the water with a rotary evaporator at 60 °C.

Synthesis of Epoxidized Castor Oil Polyol Ester (ECOPE-1). 100 g of COPE-2, 7.75 g of formic acid and 0.25 g of phosphoric acid were mixed in a four-necked round-bottomed flask that was equipped

with a mechanical stirrer, condenser pipe, thermometer and constant pressure funnel. 80 mL of hydrogen peroxide solution was dropped in the reaction in 30 min, and the solution was stirred at 60 °C for 8 h to finish the epoxidation reaction. Then the reaction mixture was separated from water with a separating funnel and washed to pH = 7 with distilled water and the water was removed with a rotary evaporator at 60 °C.

Preparation of PVC Films. 10 g of PVC was mixed with 4 g of plasticizer (DOP, ESO, COPE-1, ECOPE-1, COPE-2 and ECOPE-2, respectively) using THF as the solvent. The mixture was thoroughly agitated by mechanical stirring for 1 h followed by sonication for 10 min. The samples were then cast into Petri dishes (diameter 19 cm) and dried at ambient temperature for 7 days to remove traces of residual solvent, to obtain thin films. The content of the residual THF was explored according to references 23 and 24. The results indicated that 8–10% THF remained in the PVC after casting and that the last 3–5% was very difficult to remove after drying. The PVC blends were labeled as PVCD (PVC/DOP), PVCE (PVC/ESO), PVC1 (PVC/COPE-1), PVC2 (PVC/COPE-1), PVC3 (PVC/COPE-2) and PVC4 (PVC/ECOPE-2), and the pure PVC blend was labeled as PVC0.

Characterization. The acid value, hydroxyl value, viscosity and moisture content of synthesized products were characterized according to reference 20. The epoxy value of plasticizer was characterized according to the GB/T 1677-2008 (determinating the epoxy value of plasticizers, Chinese Industrial Standards). FT-IR spectra of castor oil based polyol ester were recorded on a Nicolet iS10 FT-IR (Nicolet Instrument Crop., USA) Fourier transform infrared spectrophotometer. The spectra were acquired in the range of 4000 to 500 cm⁻¹ at a resolution of 4 cm⁻¹. ¹H NMR spectra of castor oil based polyol ester were recorded by using an AV-300 NMR spectrometer (Bruker, Germany) at a frequency of 400 MHz with tetrametylsilane as an internal standard. The thermal ability of PVC blends was characterized in a TG209F1 TGA thermal analysis instruments (Netzsch Instrument Crop., Germany) in N₂ atmosphere (50 mL/min) at a heating rate of 10 °C/min. 5 mg of samples was put into platinum pans and scanned from 30 to 600 °C. The dynamic mechanical analysis was performed via a DMTA Q800 (TA Instruments, US) with gas cooling accessory to observe the α-transitions of the PVC blends under investigation. Rectangular samples of geometry 80 mm (L) × 10 mm (W) × 4 mm (T). The oscillatory frequency of the dynamic test was 1 Hz. The temperature was raised at a rate of 3 °C/min from –80 to +100 °C. Tensile modulus, tensile strength and elongation at break of every PVC sample were determined according GB/T 1040.1-2006 (China) under ambient conditions by using an E43.104 Universal Testing Machine (MTS Instrument Crop., China). Excellent volatility resistance was particularly important in PVC products, where specifications require minimal losses. Volatility measurements of PVC samples were carried out as follows. Weighted PVC samples (25 mm × 25 mm × 1 mm) were heated in an oven that was previously set at 120 °C for 48 h and cooled to room temperature in a desiccator for 1 h. The weight changes were measured before and after heating. The volatility rate was calculated as the ratio of the evaporated and the initial plasticizer.^{12,25} Solvent extraction tests were based on ASTM D1239-98. The test condition was restricted at a temperature of 23 ± 2 °C and 50 ± 5% relative humidity. The PVC specimens were immersed in five different solvents (distilled water, soybean oil, 10% (v/v) ethanol, 30% (w/v) acetic acid and petroleum ether). Samples were weight and kept in 200 mL of each solvent. After 24 h, the solvent extracted PVC specimens were rinsed and then wiped up. Afterward, all of the PVC specimens were dried under the test conditions in oven at 30 °C for 24 h and reweighed. The extraction loss was calculated according to the eq 1:

$$\text{weight loss (\%)} = [(W_1 - W_2)/W_1] \times 100 \quad (1)$$

where *W*₁ = initial weight of test specimen, and *W*₂ = final weight of test PVC specimen. Exudation tests of the castor oil based polyol ester plasticizers were carried out by placing a sample of PVC films between two pieces of vegetable parchment. The system (PVC film and vegetable parchment) was then placed in a drying oven at 60 °C for 48

h. Afterward, the weight increment of the vegetable parchment and the extent of the castor oil based polyol ester plasticizers exudation were calculated according to eq 1.

RESULTS AND DISCUSSION

FT-IR. The FT-IR spectra of CO, COP-1, COPE-1, ECOPE-1, COP-2, COPE-2 and ECOPE-2 are shown in Figure 3.

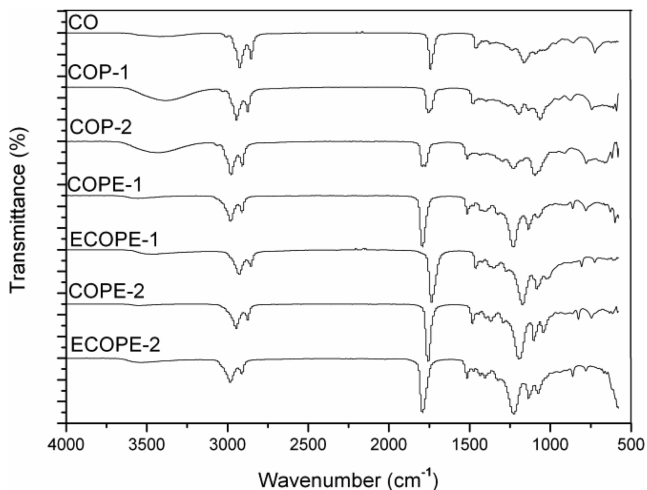


Figure 3. FTIR spectra of CO and synthesized products.

Compared with CO and COP-1, COP-2, the FT-IR spectra of COP-1 and COP-2 showed a strong and broad band at around 3500 cm^{-1} , the intensity of the band increased because many hydroxyls generated from the alcoholysis and condensation. The strong and broad band of hydroxyls disappeared in the FT-IR spectra of COPE-1 and COPE-2, and the strong absorption of the ester band appeared, implying that an esterification

reaction of C—OH of COP-1, COP-2 with acetic anhydride occurred. The epoxy group at 846 cm^{-1} appeared in the FT-IR of ECOPE-1 and ECOPE-2, and the $\text{C}=\text{C}$ double band of COPE-1, COPE-2 at around 3007 cm^{-1} disappeared, which indicated that the epoxidation reaction occurred. All of these data may suggest that expected castor oil based polyol ester was synthesized successfully.

$^1\text{H NMR}$. To verify further the chemical structure of castor oil based polyol ester, the $^1\text{H NMR}$ of COPE-1, ECOPE-1, COPE-2 and ECOPE-2 was investigated, which are shown in Figure 4A,B,C,D, respectively. From Figure 4A, the methyl protons were at $\delta = 0.89\text{ ppm}$ (peak 1), the methylene protons $[-(\text{CH}_2)_n-]$ were at $\delta = 1.15\text{ ppm}$ and $\delta = 1.3\text{ ppm}$ (peak 2 and peak 3). The bands at $2830\text{--}2960\text{ cm}^{-1}$ of methylene groups were found in the FT-IR spectrum of COPE-1 and ECOPE-1. The methylene group protons $[-(\text{CH}_2)-\text{CH}=\text{CH}-]$ (peak 5) were at $\delta = 2.0\text{ ppm}$. And the peak at $\delta = 2.3\text{ ppm}$ was assigned to $-\text{CH}_2-$ of $[-\text{O}-\text{C}-\text{CH}_2-\text{C}-\text{O}-]$ (peak 6). The peak at $\delta = 3.85\text{ ppm}$ (peak 7) was assigned to $[-\text{CH}_2-]$ connected with $[-\text{C}-\text{O}]$. The proton signals in the $5.3\text{--}5.5\text{ ppm}$ (peak in the $^1\text{H NMR}$ of COPE-1) region of the spectrum of COPE-1 associated with $-\text{CH}=\text{CH}-$ bands were replaced in the spectrum of ECOPE-1 a resonance at $\delta = 3.3\text{ ppm}$ in Figure 4B corresponding to protons on the epoxy groups, which indicated that the $-\text{CH}=\text{CH}-$ of COPE-1 bonds was reacted with hydrogen peroxide solution. The $^1\text{H NMR}$ spectra of COPE-2 and ECOPE-2 are similar to those of COPE-1 and ECOPE-1, the characteristic absorptions are labeled in Figure 4C,D. On the basis of the data from $^1\text{H NMR}$ and FT-IR, we may conclude that COPE-1, ECOPE-1, COPE-2 and ECOPE-2 were prepared.

TGA. The TGA and DTG of PVC plasticized with different plasticizers are presented in Figures 5 and 6, and the detailed parameters are summarized in Table 2. From the TGA curves of PVC blends, it could be seen that all of the PVC blends were

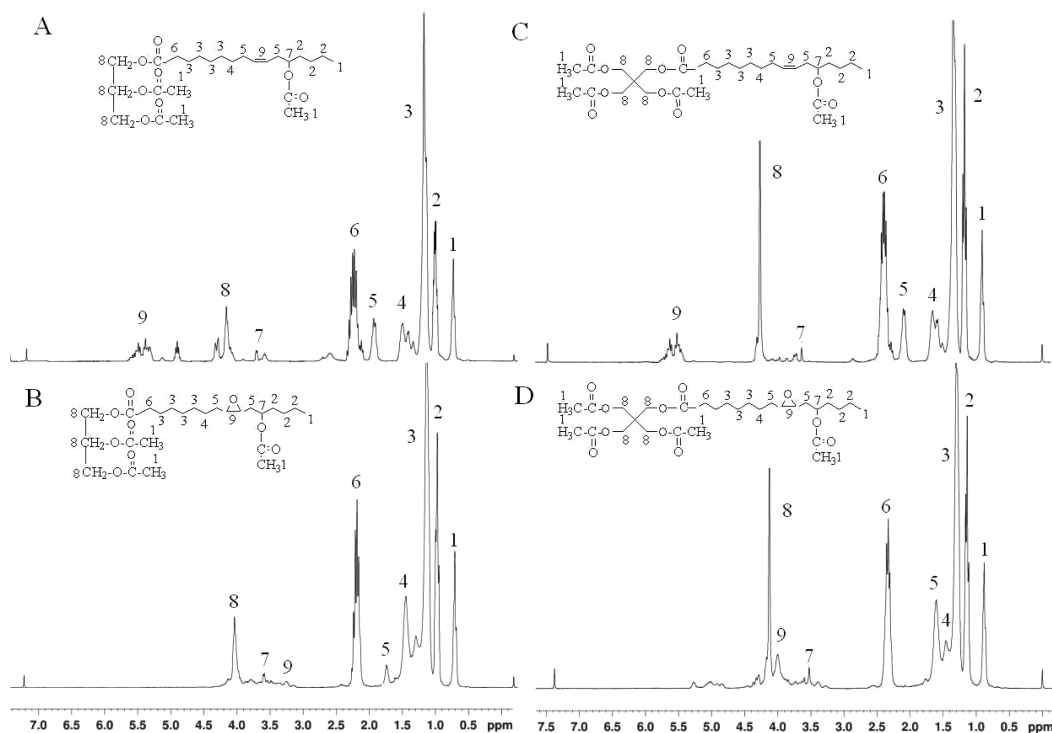


Figure 4. $^1\text{H NMR}$ spectrum of the COPE-1 (A), ECOPE-1 (B), COPE-2 (C) and ECOPE-2 (D).

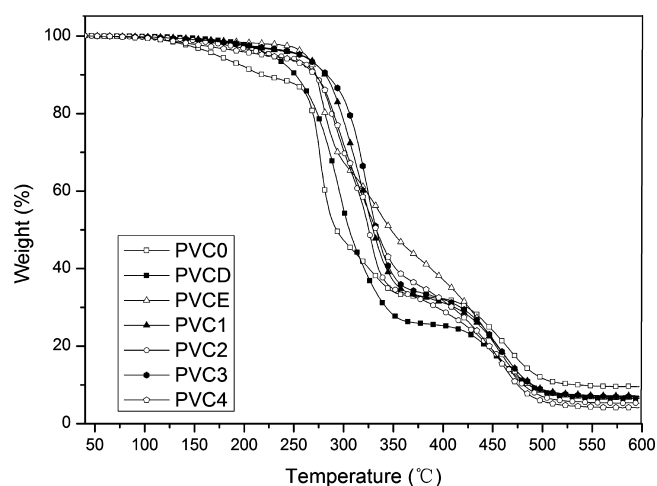


Figure 5. TGA curves of PVC blends.

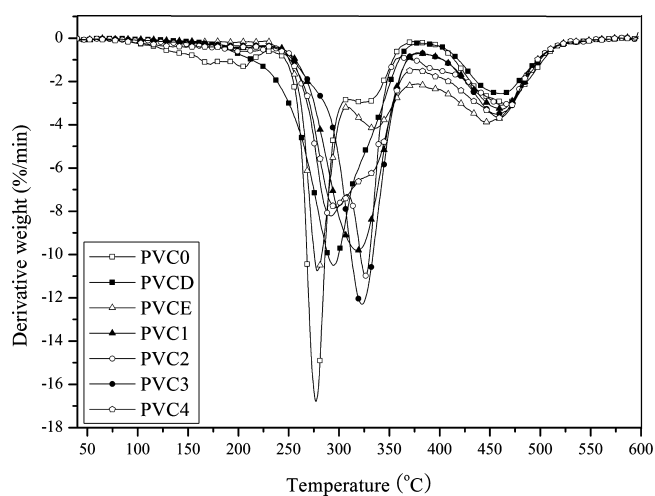


Figure 6. DTG curves of PVC blends.

Table 2. TGA and DMA Data of PVC Blends

samples	T_d (°C)	T_{10} (°C)	T_{50} (°C)	T_{P1} (°C)	T_{P2} (°C)	T_g (°C)	residue (%)
PVC0	246.9	212.8	294.6	277.1	467.2	84.2	9.63
PVCD	258.6	216.4	308.2	294.4	461.2	43.1	6.46
PVCE	266.1	246.5	346.2	278.2	448.1	46.5	6.66
PVC1	296.9	256.8	336.9	322.8	457.2	44.3	6.93
PVC2	273.8	274.3	317.1	296.0	458.5	43.5	4.13
PVC3	285.3	268.5	326.8	319.1	463.0	38.3	7.16
PVC4	272.8	294.2	324.4	326.0	460.6	33.2	5.30

thermally stable in a nitrogen atmosphere below 130 °C and exhibited a two-stage thermal degradation process above that temperature. The first degradation at about 270–320 °C is corresponding to the elimination of a large amount of HCl. The second stage at about 440–480 °C is attributed to cross-linking containing the C=C bond. The process of thermal degradation of polyenes involves cyclization and splitting of chains.^{11,26,27}

The thermal performance data including decomposition temperature (T_d), the mass loss of 10% (T_{10}), the mass loss of 50% (T_{50}) and the maximum weight-loss temperature rate (T_{P1} and T_{P2}) are summarized in the Table 2. T_d , T_{10} , T_{50} and T_{P1} values of PVC plasticized with COPE-1, ECOPE-2, COPE-2 and ECOPE-2 were higher than those of ESO and DOP. It

indicated that COPE-1, ECOPE-1, COPE-2 and ECOPE-2 could improve the thermal stability of PVC blends than that of ESO and DOP. Because more ester bonds connected to the structure of castor oil polyol ester and ester bonds with higher thermal stability limited the decomposition of those segments with lower-thermal-stability chain segments, thereby increasing the thermal stability of PVC blends. And the amount char residue of sample PVC0, PVCD, PVCE, PVC1, PVC2, PVC3 and PVC4 is 9.63, 6.46, 6.66, 6.93, 4.43, 7.16 and 5.30%, respectively. The char residue of PVC plasticized with DOP is more than that of the other plasticizers, indicating that COPE-1, ECOPE-1, COPE-2 and ECOPE-2 could decrease char residue of PVC blends than DOP. From these data, we could conclude that the castor oil based polyol ester could improve the thermal stability and reduce the amount of char residual of PVC blends.

DMA. The lower glass transition temperatures (T_g) of PVC blends indicate that the compatibility of PVC and the plasticizer is more excellent.²⁸ The dynamic mechanical property of PVC blends was measured by DMA, and the T_g values are shown in Table 2. Figure 7 shows DMA curves of all PVC blends. It can

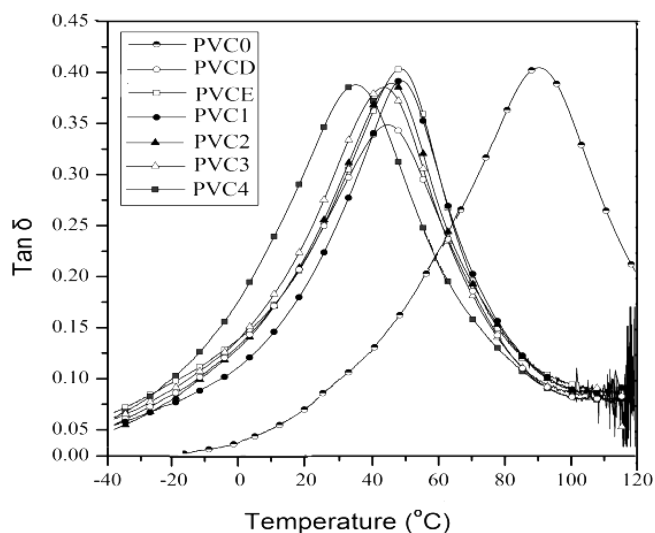


Figure 7. DMA curves of PVC blends.

be seen that all of the plasticized PVC blends showed only a tan δ peak, indicating that the four plasticizers were compatible with PVC. The T_g value for PVC0, PVCD, PVCE, PVC1, PVC2, PVC3 and PVC4 is 84.2, 43.1, 46.5, 44.3, 43.5, 38.2 and 33.2 °C, respectively, which indicated the plasticizer could reduce the T_g of PVC blends. With increasing of ester bands in the chemical structure of castor oil based polyol ester, the T_g values of PVC4 are lower than those of the other plasticizers. Moreover, more ester bands existed in the chemical structure of the plasticizer, easier for compatibility between PVC and the plasticizer. Compatibility is a key factor to evaluate the plasticizer, because the final mechanical properties of PVC blends depend on the compatibility. A plasticizer behaves similar to a solvent when mixed into a polymer and results in the lowering of the T_g and by this way influences its flexibility. Ziska et al. and Mohamed et al. reported that the appearance of a single T_g was often used as a criterion for blend compatibility.^{29–31} The results indicated that the plasticizing effect on PVC of COPE-2 and ECOPE-2 is better than that of the other plasticizers.

Tensile Tests. The elongation at break, tensile strength and modulus of elasticity of PVC blends are presented in Table 3.

Table 3. Tensile Properties of PVC Blends

sample	modulus of elasticity (mPa)	elongation at break (%)	tensile strength (mPa)
PVC0	1198.32	167.52	42.48
PVCD	21.6	452.85	30.14
PVCE	15.16	427.55	36.99
PVC1	66.06	521.6	30.99
PVC2	74.22	524.63	23.3
PVC3	99.66	435.89	33.05
PVC4	82.36	475.72	27.69

PVC0 showed a lower elongation at break of 167.52% and higher tensile strength of 42.48 mPa compared with the other samples. PVC2 and PVC4 presented higher elongation at break and lower tensile strength than PVCE, PVC1 and PVC3. PVC2 and PVC4 contained ECOPE-1 and ECOPE-2, which indicated that the plasticizer exhibited a more efficient plasticizing effect on PVC with increasing of ester bands and epoxy bonds in their chemical structure. And the PVC4 showed a higher elongation at break and lower tensile strength than PVCD, indicating that the plasticizing effect of ECOPE-2 on PVC is more efficient than that of DOP.

Exudation Test. In the exudation test, plasticized PVC blends show the exudation loss of DOP, ESO, COPE-1, ECOPE-1, COPE-2 and ECOPE-2 is 0.104, 0.083, 0.062, 0.039, 0.021 and 0.016% during the experimental period, indicating that all of the plasticizers were fully compatible with PVC.

Migration Stability. The migration stability of the different plasticizer in PVC blends was investigated by the leaching tests using five different solvents, and the results are presented in Figure 8. Every value was the average of the values for five

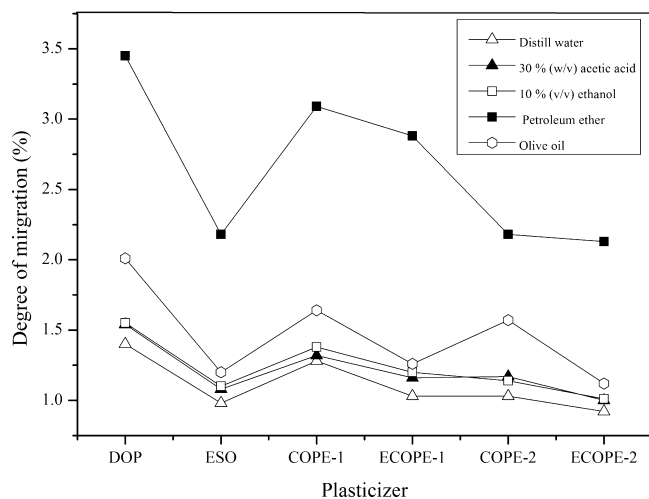


Figure 8. Degree of migration of plasticizer.

specimens. PVC blends samples showed different migration resistance when they were immersed in different solvents. All of the plasticizers presented lower migration resistance in petroleum ether, because all of the plasticizers are organic solvents. It is impressive to observe that the migration of a high molecular weight plasticizer was obviously lower in these five different solvents than that of low molecular weight plasticizers. As can be seen from Figure 8, DOP exhibited the lowest

migration resistance but ESO presented the highest migration resistance. With the increasing of the molecular weight of castor oil based polyol ester, the migration stability is similar to ESO. The higher migration resistance of PVC plasticized with castor oil based polyol ester indicated that they are with potential application value in food packing, children toys and medical devices.

Volatility Stability. The volatility stability of all plasticizers was investigated, and the results are shown in Figure 9. The

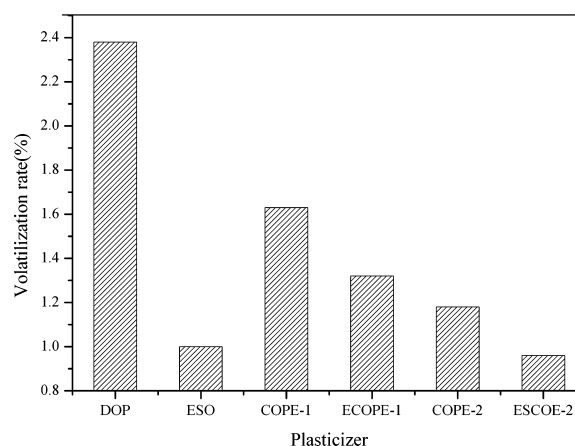


Figure 9. Volatility stability of plasticizer.

volatile mass of DOP, ESO, COPE-1, ECOPE-1, COPE-2 and ECOPE-2 in the PVC blends is 2.38, 1, 1.63, 1.32, 1.18 and 0.96%, respectively. The trend is similar to that of migration stability. The results further illustrate that the high molecular weight and more ester bands could improve the migration stability and volatility of the plasticizer.

CONCLUSIONS

In this study, we synthesized a series of environmental friendly plasticizer castor oil based polyol esters. Their chemical structure was characterized with FT-IR and ^1H NMR. Properties of PVC blends plasticized with the synthesized castor oil polyol ester as the main plasticizer were investigated and compared with those of the commercial plasticizers DOP and ESO. TGA showed that castor oil based polyol ester could improve the thermal stability and reduce the amount of char residual of PVC blends. DMA illustrated that the plasticizing effect of COPE-2 and ECOPE-2 on PVC is better than that of DOP, ESO, COPE-2 and ECOPE-1. Tensile tests showed that the plasticizing effect of ECOPE-2 on PVC is more efficient than DOP. Both migration stability and volatility stability of tests showed that with the increasing of the molecular weight of castor oil based polyol ester, the migration stability and volatility stability enhanced. On the basis of the above excellent performance of castor oil based polyol esters, they may have potential application value in food packing, children toys and medical devices.

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Notes

The authors declare no competing financial interest.

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