

Green plasticizers derived from soybean oil for poly(vinyl chloride) as a renewable resource material

Puyou Jia*, Meng Zhang**,†, Lihong Hu**, and Yonghong Zhou*,†

*Institute of Chemical Industry of Forest Products, Chinese Academy of Forest (CAF), Nanjing 210042, P. R. China

**Institute of New Technology of Forestry, Chinese Academy of Forest (CAF), Beijing 100091, P. R. China

(Received 1 April 2015 • accepted 11 October 2015)

Abstract—Vegetable oil based plasticizers have potential use as nontoxic and sustainable plasticizer and as replacements for commonly used phthalate plasticizers. In this study, novel soybean oil based polyol esters (derived from glycerin or pentaerythritol, of which two were acetylated and two were additionally epoxidized) were synthesized and characterized with GPC, FT-IR and ¹H NMR. Properties of poly (vinyl chloride) (PVC) plasticized with different soybean oil based polyol ester as main plasticizer were evaluated and compared to that of traditional plasticizers dioctyl phthalate (DOP) and epoxidized soybean oil (ESO). It has been proved that thermal stability of PVC blends could be improved by soybean oil based polyol ester plasticizers. Plasticizing effect of pentaerythritol derived soybean oil polyesters on PVC is better than that of DOP, ESO, and glycerin derived soybean oil polyesters. Tests of migration stability showed that with the increasing of the molecular weight, branching degree of molecular and ester bands of soybean oil based polyol ester, the migration stability was enhanced. This study may lead to the development of new type of PVC materials using soybean oil based polyol ester as main plasticizer.

Keywords: Poly (vinyl chloride), Soybean Oil, Plasticizer, Thermal Property, Migration Resistance

INTRODUCTION

Poly (vinyl chloride) (PVC) is a versatile material with an extensive range of applications such as food packaging, biomedical, children's toys, etc [1]. PVC materials present flexibility, softness, distensibility and workability when plasticized with plasticizers. Phthalate plasticizers are the most commonly used plasticizers that are easily released from the PVC matrix because of low molar mass. When they are used in some applications such as children's toys, medical devices and food packaging, the loss of plasticizers not only causes changes in long-term properties of products but also has a potential biological effect on the human body [2-4]. Since the 1940s, the toxicity of phthalates has been investigated. After the 1990s, people began to be concerned by the negative effect of phthalates on animals, including adverse effects on animals' liver, heart, kidneys, lungs, and other organs [5]. Furthermore, most of these plasticizers are derived from petroleum. With the depletion of petrochemical resource and the rising price of fossil oil, vegetable oil has been focused on substituting with petrochemical resource to synthesize chemical products. Recently, there has been growing interest in the use of plasticizers obtained from vegetable oil because of advantages of non-toxic, environmental, biodegradable and renewable raw materials. Recent publications reported the synthesis and possible application of vegetable oil based plasticizers such as epoxidized safflower oil [6], epoxidized neem oil [7], epoxidized linseed oil [8], epoxidized soybean oil [9,10], soybean oil fatty acid methyl

ester [11], benzyl ester of dehydrated castor oil fatty acid [12], soybean oil based polyol [13], epoxidized broccoli oil [14]. A significant body of work has shown that epoxidized soybean oil can indeed be used as primary/single plasticizer for PVC, provided a suitable heat stabilizer is included in the formulation [15-17]. We have synthesized glyceryl monooleate-based polyester plasticizer [18] and phosphorous-containing plasticizer based on vegetable oil [19-22]. The glyceryl monooleate-based polyester plasticizer is efficient to improve the thermal stability of PVC blends; the high migration stability can keep the property of PVC products for a long time. But the glyceryl monooleate-based polyester plasticizer must be cooperated with phthalates plasticizer to blend with PVC which limits its application. Phosphorous-containing plasticizer based on vegetable oil can improve thermal stability, flame retardant performance and mechanical property of PVC blends. They are potential and functional plasticizers for PVC.

The current work focuses on synthesizing soybean oil based polyol ester plasticizers such as acetyl soybean oil polyol ester (SOPE-1, SOPE-2) and epoxy acetyl soybean oil polyol ester (ESOPE-1 and ESOPE-2), and investigating their plasticizing effect on PVC as main plasticizer. Their chemical structure was characterized using FT-IR, ¹H NMR and GPC. Thermal property, mechanical property and crystallinity of PVC plasticized with synthesized plasticizers were explored. Migration resistance and leachability of these plasticizers were investigated.

EXPERIMENTAL

1. Materials and Chemicals

Epoxidized soybean oil (ESO, chemical pure) with oxirane oxy-

†To whom correspondence should be addressed.

E-mail: yhzhou777@sina.com, zhangmeng82@163.com

Copyright by The Korean Institute of Chemical Engineers.

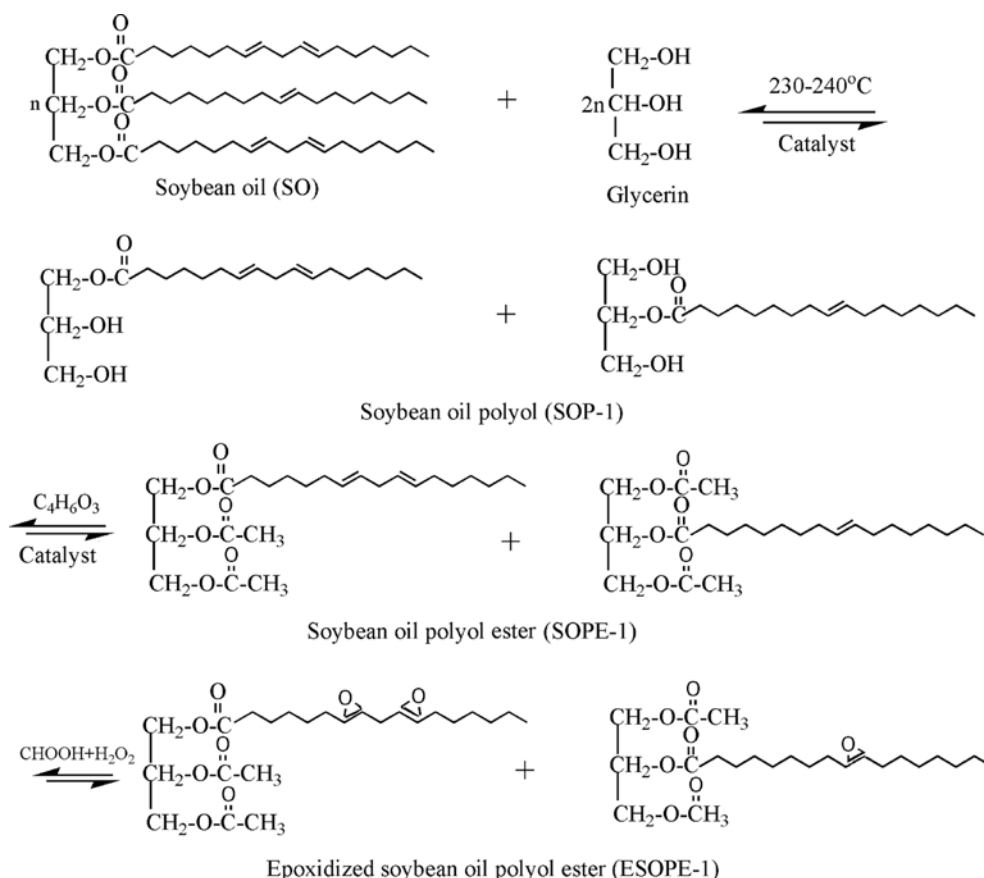


Fig. 1. Synthesis of ESOPE-1.

gen content 5-6%, and iodine value 0-6 g I_2 /100 g, pentaerythritol, glycerol, phosphoric acid, formic acid, 30% hydrogen peroxide solution, acetic anhydride, sodium hydroxide and dioctyl phthalate (DOP) were provided by Nanjing Chemical Reagent Co., Ltd. (China). All of the reagents were analytical reagent. Polyvinyl chloride (PVC) was supplied by Hanwha (South Korea) with K value 65.0 and degree of polymerization 1300 ± 100 . Soybean oil (SO, edible grade) provided by Arowana Co., Ltd. (China).

2. Method

2-1. Synthesis of Soybean Oil Polyol (SOP-1)

A four-necked round-bottom flask equipped with a mechanical stirrer, condenser pipe, thermometer and provision for nitrogen flushing was charged with soybean oil 500 g, sodium methoxide 0.18 g, triethylamine 3.6 g. The temperature was raised to $230-240^{\circ}\text{C}$ after continuous nitrogenation for 20 min. Then 122 g of glycerol was taken in the mixture. The temperature was maintained at $230-240^{\circ}\text{C}$ for 2.5 h [18,19,23,24].

2-2. Synthesis of Soybean Oil Polyol Ester (SOPE-1)

200 g of SOP-1 and 160 g of acetic anhydride were mixed in a three-necked round-bottom flask equipped with a mechanical stirrer, condenser pipe and thermometer. Stirred at 140°C for 1 h to finish esterification. Then the reaction mixture was washed thrice with distilled water and the water removed with a rotary evaporator at 60°C .

2-3. Synthesis of Epoxidized Soy Bean Oil Polyol Ester (ESOPE-1)

200 g of SOPE-1, 15.5 g of formic acid and 0.50 g of phosphoric

acid were mixed in a four-necked round-bottom flask equipped with a mechanical stirrer, condenser pipe, thermometer and constant pressure funnel. 150 ml hydrogen peroxide solution was dropped in the reaction in 30 min and stirred at 60°C for 8 h to finish epoxidation. Then the reaction mixture was separated from water with separating funnel and washed thrice with distilled water, then the water removed with a rotary evaporator at 60°C . Fig. 1 showed that synthetic route of ESOPE-1.

2-4. Synthesis of Soybean Oil Polyol (SOP-2)

200 g of soybean oil, 60 g of pentaerythritol and 1.30 g of calcium hydroxide were placed together in a four-necked round-bottom flask equipped with a mechanical stirrer, condenser pipe, thermometer and provision for nitrogen flushing. The reaction mixture was heat to 230°C for 3.5 h.

2-5. Synthesis of Soybean Oil Polyol Ester (SOPE-2)

100 g of SOP-2 and 130 g of acetic anhydride was mixed in a three-necked round-bottom flask which was equipped with a mechanical stirrer, condenser pipe and thermometer. Stirred at 140°C for 1 h to finish esterification. Then the reaction mixture was washed thrice with distilled water and the water removed with a rotary evaporator at 60°C .

2-6. Synthesis of Epoxidized Soybean Oil Polyol Ester (ESOPE-2)

100 g of SOPE-2, 7.75 g of formic acid and 0.25 g of phosphoric acid were mixed in a four-necked round-bottom flask equipped with a mechanical stirrer, condenser pipe, thermometer and constant pressure funnel. 80 ml hydrogen peroxide solution was dropped

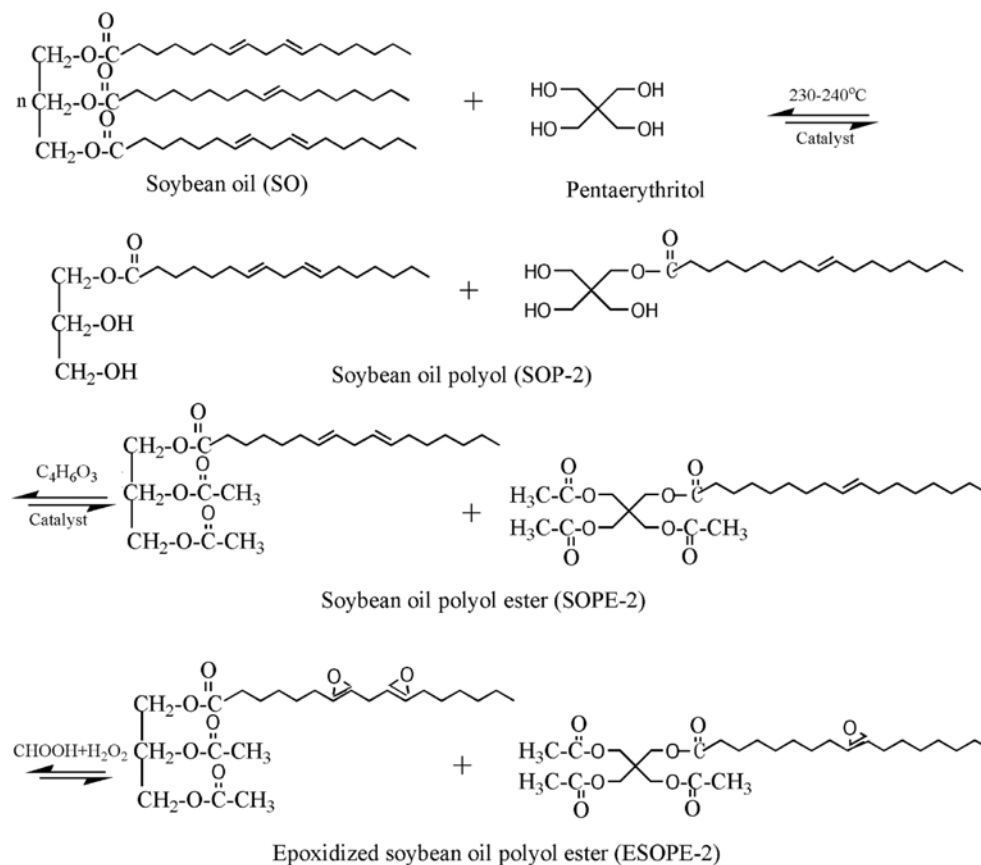


Fig. 2. Synthesis of ESOPE-2.

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 separating funnel and washed thrice with distilled water, then the water removed with a rotary evaporator at 60 °C. Fig. 2 showed that synthetic route of ESOPE-2.

2-7. Preparation of PVC Blends

20 g PVC was mixed with 8 g plasticizer (DOP, ESO, SOPE-1, ESOPE-1, SOPE-2 and ESOPE-2, respectively) using 300 ml THF as the solvent. The mixture was thoroughly agitated using a mechanical agitator at 160 rpm for 1 h at 60 °C followed by sonication for 10 min until the mixture presented clear and transparent. 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 and to obtain thin films [1,25-27]. The thickness of the cast films were around 3-5 mm. The residual THF were investigated according to the H. Lai et al's study [28]. The results indicated that 3-5% THF remained in the PVC blends after casting and drying. The polymer and blends that were evaluated are identified as follows: PVC0 (no plasticizer); PVCD (DOP as plasticizer); PVCE (ESO as plasticizer); PVC1 (SOPE-1 as plasticizer); PVC2 (ESOPE-1 as plasticizer); PVC3 (SOPE-2 as plasticizer); and PVC4 (ESOPE-2 as plasticizer). Note that no heat stabilizer was added.

3. Materials Characterization

3-1. FT-IR

FT-IR spectra of synthesized plasticizers were recorded on a Nicolet iS10 FT-IR (Nicolet Instrument Corp., USA) Fourier transformed

infrared spectrophotometer. The plasticizer samples were sandwiched between two plates of KBr. The spectra were acquired in the range of 4,000 cm^{-1} to 500 cm^{-1} at a resolution of 4 cm^{-1} .

3-2. GPC

Molecular weight of SO, SOP-1 and SOP-2 was measured by using an Efficient gel chromatograph made by Waters, USA at 30 °C (flow rate: 1 ml/min, column: mixed PL gel 300×718 mm, 25 μm) using THF as solvent.

3-3. 1H NMR

1H NMR spectra of obtained plasticizers were recorded by an AV-300 NMR spectrometer (Bruker, Germany) at a frequency of 300 MHz with tetrametylsilane as an internal standard.

3-4. TGA

TGA was by a TG209F1 TG thermal analysis instrument (Netzsch Instrument Corp., German) in N_2 atmosphere (50 ml·min $^{-1}$) at a heating rate of 10 °C·min $^{-1}$. The samples was measured in a platinum pan with a mass of about 5 mg and scanned from 40 °C to 800 °C.

3-5. DMA

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 (L)×10 (W)×4 (T) mm 3 . The oscillatory frequency of the dynamic test was 1Hz. The temperature was raised at a rate of 3 °C/min in the range of -80 °C-100 °C.

3-6. XRD

The crystallinity data were obtained via X-ray diffraction (XRD)

with a D8 FOCUS (BRUKER, German) operated at 45 kV and 40 mA using Cu-K α radiation with a graphite diffracted beam monochromatic. Data were acquired in a 2 theta scale from 10°-80°.

3-7. Exudation Test

Exudation of synthesized plasticizers was evaluated by placing a sample of PVC blends between two pieces of parchment paper. The system (PVC blends+two pieces of parchment paper) was then placed in a drying oven at 40 °C for 48 h. After this period, the weight increment of the paper was determined and the extent of plasticizer exudation was calculated.

3-8. Migration Stability Tests

Leaching tests were based on ASTM D1239-98. The test conditions were restricted at a temperature of 23±2 °C and 50±5% relative humidity. The PVC specimens were immersed in five different solvents (distilled water, olive oil, 10% (v/v) ethanol, 30% (w/v) acetic acid and petroleum ether). Samples were weighed and kept in 200 mL of each solvent. After 24 h, the solvent extracted PVC specimens were rinsed with isooctane and then wiped up using vegetable parchment [29-32]. 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 Eq. (1): Weight loss = $[(W_1 - W_2)/W_1] \times 100$, where W_1 = initial weight of test specimen, and W_2 = final weight of test PVC specimen [33].

3-10. Tensile Tests

Tensile modulus, tensile strength, and elongation at break were determined according GB/T 1040.1-2006 (China) under ambient conditions, using E43.104 Universal Testing Machine (MTS Instrument Corp., China). The reported values were the average of six samples.

RESULTS AND DISCUSSION

1. GPC

The GPC spectra of SO, SOP-1 and SOP-2 are presented in Fig. 3. From the curves of SOP-1 and SOP-2, the molecular weights of 249 g/mol and 269 g/mol represented mono-glyceride, and the molecular weights of 521 g/mol and 563 g/mol represented di-glyceride, while there was only a single peak of 912 g/mol in SO spectra.

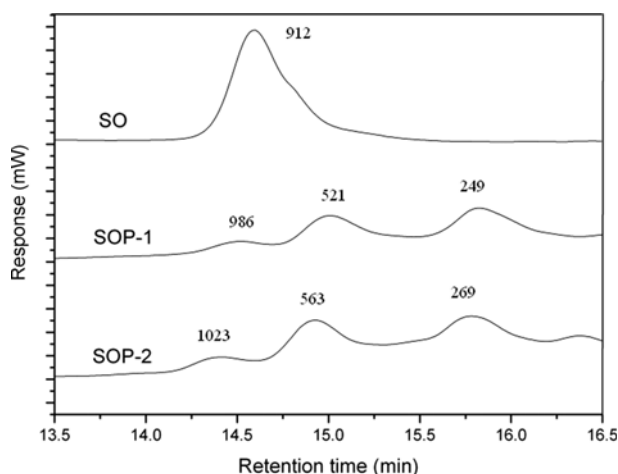


Fig. 3. The GPC spectra of SO, SOP-1 and SOP-2.

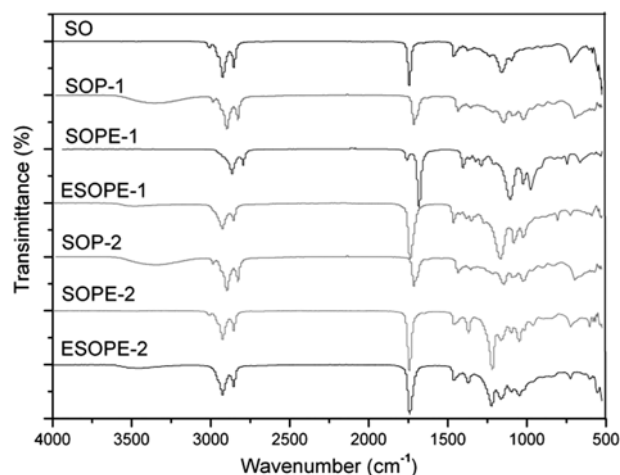


Fig. 4. FTIR spectra of SO and synthesized products.

These results indicated the alcoholysis reaction of SO and polyol (glycerol, pentaerythritol) had occurred [24].

2. FT-IR

The spectra of SO, SOP-1, SOPE-1, ESOPE-1, SOP-2, SOPE-2 and ESOPE-2 are compared in Fig. 4. In the spectrum of SO, several characteristic peaks are indicated in the spectrum of SO, the band at 3,008.67 cm^{-1} , which is assigned to the absorption of =C-H bonds, methyl and methylene groups (2,922.54 cm^{-1} and 2,852.95 cm^{-1}), ester carbonyl groups (1,743.40 cm^{-1}), and the band at 1,657.78 cm^{-1} , which is assigned to the absorption of -C=C- bonds. The FT-IR spectra of SOP-1 and SOP-2 show a strong and broad band between 3,468 cm^{-1} , the intensity of the band increased because many hydroxyls were generated from the alcoholysis and condensation. The strong and broad band of hydroxyls disappeared in the FT-IR spectra of SOPE-1 and SOPE-2, and a strong absorption of ester band at around 1,740 cm^{-1} appeared, implying that an esterification reaction of C-OH of SOP-1, SOP-2 with acetic anhydride occurred. To epoxy group at 961 cm^{-1} appeared in the FT-IR of ESOPE-1 and ESOPE-2, and the -C=C- double band of SOPE-1, SOPE-2 at around 3,017 cm^{-1} disappeared, which indicated that

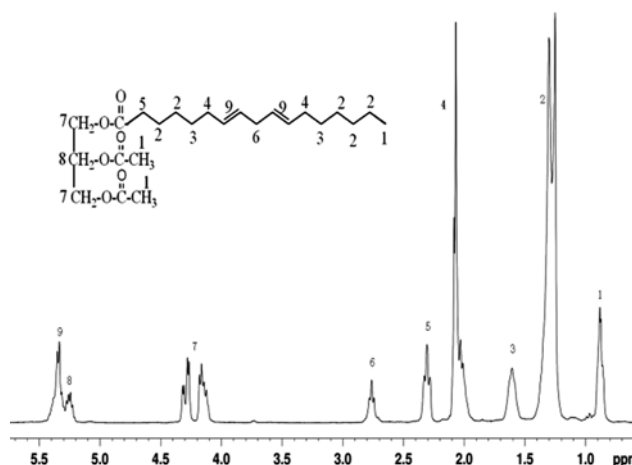


Fig. 5. ^1H NMR spectrum of SOPE-1.

the epoxidation reaction occurred. All of these data may suggest that expected soybean oil based polyol ester was synthesized successfully.

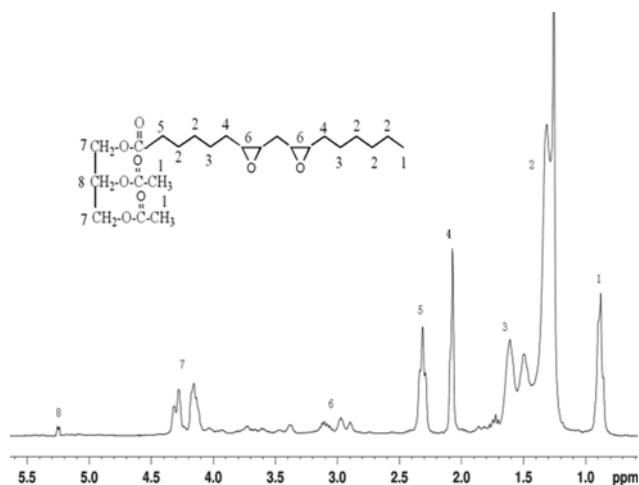


Fig. 6. ^1H NMR spectrum of ESOPE-1.

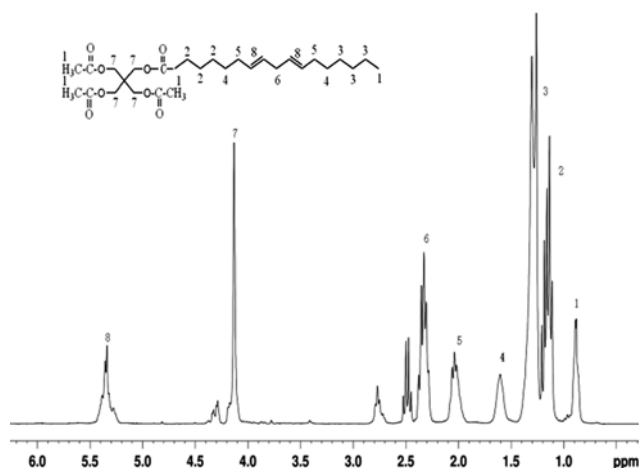


Fig. 7. ^1H NMR spectrum of SOPE-2.

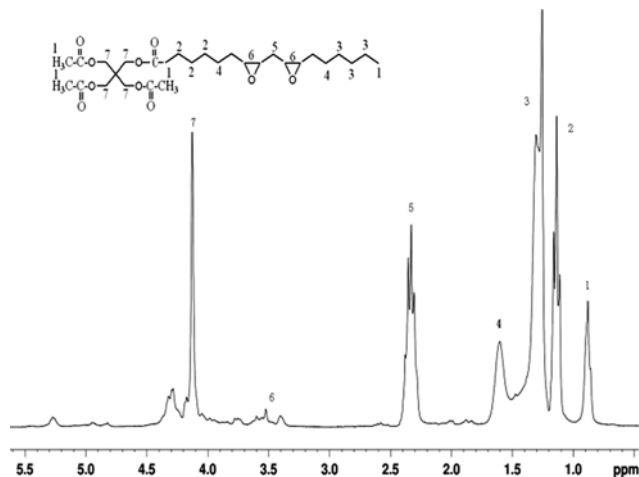


Fig. 8. ^1H NMR spectrum of ESOPE-2.

3. ^1H NMR

Fig. 5, Fig. 6, Fig. 7 and Fig. 8 illustrate the ^1H NMR of SOPE-1, ESOPE-1, SOPE-2 and ESOPE-2, respectively. As indicated in the spectrum of these synthesized products, the peak at 0.89 ppm corresponds to the terminal methyl protons of fatty acids ($-\text{CH}_3-$) (peak 1 in the Fig. 5, Fig. 6, Fig. 7 and Fig. 8, respectively), the multiplets around 4.2–4.4 ppm correspond to the methylene protons of glycerol (peak 7 in the Fig. 5 and Fig. 6, respectively); these peaks are always taken as references and could be used as internal standards to quantitatively characterize the content of certain groups, because the intensity of the peak should not be altered during the reaction [34]. In Fig. 5 and Fig. 6, the methylene protons $[-(\text{CH}_2)_n-]$ were at $\delta=1.3$ ppm (peak 2). The methylene group protons $[-(\text{CH}_2)-\text{CH}=]$ (peak 4) were at $\delta=2.0$ ppm. And the peak at $\delta=2.3$ ppm was assigned to $-\text{CH}_2-$ of $[-\text{O}-\text{C}-\text{CH}_2-\text{C}-\text{O}-]$ (peak 5). The peak $\delta=5.3$ ppm (peak 8) was assigned to $[-\text{CH}_2-]$ connected with $[-\text{C}-\text{O}]$. The proton signals in the 5.4 ppm (peak in the ^1H NMR of SOPE-1) region of the spectrum of SOPE-1 associated with $-\text{CH}=\text{CH}-$ bands were replaced in the spectrum of ESOPE-1 a resonance at $\delta=3.2$ ppm (peak 6 in the spectrum of ESOPE-1) corresponding to protons on the epoxy groups, which indicated that the $-\text{CH}=\text{CH}-$ of SOPE-1 bonds reacted with hydrogen peroxide solution. The ^1H NMR spectrum of SOPE-2 and ESOPE-2 are similar to that of SOPE-1 and ESOPE-1, all of the characteristic absorption was labeled in Fig. 7 and Fig. 8. From the FT-IR and ^1H NMR of synthesized soybean oil based polyol ester, we can draw a conclusion that the SOPE-1, ESOPE-1, SOPE-2 and ESOPE-2 was obtained.

4. TGA

TGA of PVC plasticized with DOP, ESO, SOPE-1, ESOPE-1, SOPE-2 and ESOPE-2 was carried out. The TGA curves of all the PVC blends showed two degradation steps, the first step of the degradation in the temperature range of 270–320 $^{\circ}\text{C}$ is corresponding to the elimination of a large amount of HCl with some benzene traces. The second stage at about 440–480 $^{\circ}\text{C}$ is attributed to formation of conjugated unsaturation that resulted from elimination of HCl from adjacent carbon atoms. The process of thermal degradation of polyenes involves cyclization and splitting of chains [35–37]. Table 1 summarizes the thermal property data of plasticized PVC blends, including 5%, 10%, 15% and 50% weight-loss temperature (T_5 , T_{15} and T_{50}). From Table 1, T_5 , T_{15} and T_{50} of all plasticized PVC are higher than that of PVC0. T_5 , T_{15} and T_{50} of PVC1, PVC2, PVC3 and PVC4 are higher than that of PVCD and PVCE. We may conclude that all of the plasticizer used in the study could improve the thermal stability of PVC blends, and SOPE-1,

Table 1. TGA and DMA data of PVC blends

Sample	T_5 ($^{\circ}\text{C}$)	T_{15} ($^{\circ}\text{C}$)	T_{50} ($^{\circ}\text{C}$)	T_g ($^{\circ}\text{C}$)
PVC0	176.2	254.9	294.6	84.2
PVCD	214.3	261.4	308.2	43.1
PVCE	227.9	276.3	346.2	47.5
PVC1	256.3	289.8	338.6	44.6
PVC2	233.7	282.0	320.1	42.2
PVC3	253.9	310.1	326.8	44.0
PVC4	251.1	295.2	338.3	34.3

ESOP-1, SOPE-2 and ESOP-2 improved the thermal stability of PVC blends better than that of ESO and DOP. In the initial stages of decomposition, ESO behaved worse than the other soybean oil based plasticizers. We inferred that the reasons are that, first, more epoxy groups connect to the chemical structure of ESO than that of the other soybean oil based plasticizers, epoxy group is easy to react and decompose at low temperature; second, the relative content of the ester bond of ESO was less than that of the other soybean oil based plasticizers. Because more ester bonds existed in the structure of soybean 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 [24]. Consequently, ESO behaved worse than the other soybean oil based plasticizers in the early stages of decomposition. Furthermore, PVC3 and PVC4 were not too different in performance, PVC1 and PVC2 exhibited significantly different results. T_5 and T_{15} of PVC1 are higher than that of the PVC2; in the meantime, T_5 and T_{15} of PVC3 is higher than that of the PVC4. These results indicated that the existence of epoxy groups had adverse effect on the thermal stability of PVC materials. In the later stages of decomposition, ESO behaved better than the other soybean oil based plasticizers. We inferred that more olefinic bonds existed in the chemical structure of ESO than the other soybean oil based plasticizers, which are harder to thermally decompose than saturated bond.

5. DMA

The glass transition temperature (T_g) of PVC blends was measured by DMA. The values are shown in Table 1. All of the plasticized PVC blends showed only a $\tan \delta$ peak indicated that SOPE-1, ESOP-1, SOPE-2 and ESOP-2 were compatible with PVC. All the plasticizers resulted in decreasing the T_g of PVC blends. With increasing of ester bands in the chemical structure of soybean oil based polyol ester, T_g values of PVC4 presented more lower that of the other plasticizers. The lower glass transition temperature (T_g) of PVC blends indicated that the compatibility of PVC and the plasticizer is excellent [38]. More ester bands existed in the chemical structure of plasticizer, for easier compatibility between PVC and plasticizer. Compatibility is a key factor to evaluate the plasticizer,

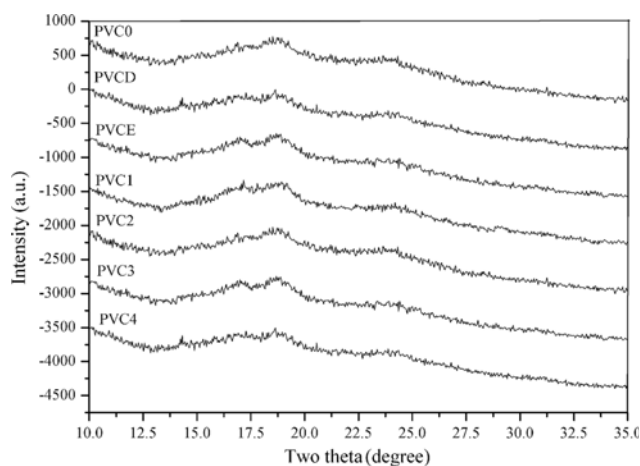


Fig. 9. XRD curves of PVC blends.

because the final mechanical properties of PVC blends depend on the compatibility.

6. XRD

Fig. 9 presents XRD diffractograms of PVC blends. XRD analysis is employed to determine the structure, complexation and crystallization of the polymer matrix [39,40]. From the corresponding angle of the characteristic peaks and applying Bragg's Law ($n\lambda = 2d\sin\theta$), for λ of 1.542 Å, the interlamellar basal distances (d) could be calculated. The diffractograms showed two characteristic peaks at $2\theta \sim 18.2^\circ$ and 24.6° , which correspond to interlamellar basal distances of 0.49 Å and 3.62 Å, respectively. According the XRD diffractograms, no difference could be observed in the crystalline of the PVC0 and PVCD, PVCE, PVC1, PVC2, PVC3 and PVC4. The results show that DOP, ESO, SOPE-1, ESOP-1, SOPE-2 and ESOP-2 cannot change the crystallinity of PVC blends.

7. Exudation Test

Exudation test of PVC blends was investigated accurately; the mass loss of all plasticized PVC blends during the experimental period showed less than 0.1%, indicating that all of the plasticizers were fully compatible with PVC.

8. Migration Stability

Fig. 10 shows the extraction loss of different plasticizer by five kinds of solvents from PVC blends. The test methods were designed to simulate each representative environment for plasticizer migration into different contacting media. Every value was the average of the values for five specimens. From Fig. 10, all of the plasticizers show lower migration resistance in petroleum ether, because all of the plasticizers are organic solvent. Migration amount of high molecular weight plasticizers was obviously less into these five different solvents than that of low molecular weight plasticizer in all five different solvents. Because the degree of branching of high molecular weight plasticizers (ESO, SOPE-2 and ESOP-2) is higher than low molecular weight plasticizers (DOP, SOPE-1 and ESOP-1), and more ester bands existed in the high molecular weight plasticizers (SOPE-2 and ESOP-2) is higher than low molecular weight plasticizers (DOP, SOPE-1 and ESOP-1). DOP exhibited the lowest migration resistance, but ESO presented the highest migration resistance. With the increasing of the molecular weight and ester bands

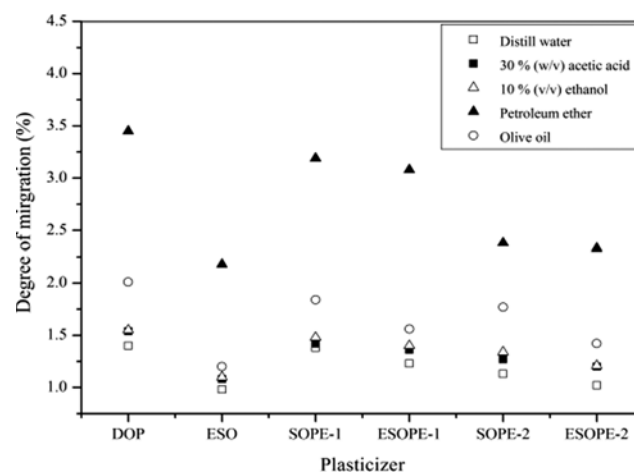


Fig. 10. Degree of migration of plasticizer.

Table 2. Tensile properties of PVC blends

Sample	Modulus of elasticity (Mpa)	Elongation at break (%)	Tensile strength (MPa)
PVC0	1198.32	167.52	42.48
PVCD	21.60	452.85	30.14
PVCE	15.16	427.55	36.99
PVC1	230.47	442.58	30.42
PVC2	267.61	598.79	30.10
PVC3	98.81	520.82	28.16
PVC4	287.93	537.82	26.60

of soybean oil based polyol ester, the migration stability is similar to ESO. The higher migration resistance of PVC plasticized with soybean oil based polyol ester will lead to the development of new type of PVC products using soybean oil based polyol ester as main plasticizer.

Tensile strength, elongation at break and modulus of elasticity of PVC blends depend on the resin and plasticizers used in their composition. Hence, these properties are a good way to evaluate the efficiency of plasticizers. The tensile strength along with elongation at break and modulus of elasticity of PVC blends are presented in Table 2. PVC0 shows a lower elongation at break of 167.52% and higher tensile strength of 42.48 MPa than that of the other samples. PVC3 and PVC4 show higher elongation at break and lower tensile strength than PVCD, PVCE, PVC1 and PVC2. Elongation at break and tensile strength of PVCD are similar to that of PVC1 and PVC2. The lower tensile strength and higher elongation at break present more effective plasticizing effect. Hence, plasticizing effect of SOPE-2 and ESOPE-2 on PVC is more efficient than that of DOP, ESO, SOPE-1 and ESOPE-1, and plasticizing effect of SOPE-1 and ESOPE-1 on PVC is similar to DOP. In terms of modulus of elasticity, which is also a reflection of plasticization efficiency, ESO seems to be the most efficient plasticizer.

CONCLUSIONS

This article describes the synthesis and application of novel soybean oil based polyol ester plasticizers. Properties of poly (vinyl chloride) (PVC) plasticized with different soybean oil based polyol ester as main plasticizer have been evaluated and compared to that of traditional plasticizers dioctyl phthalate (DOP) and epoxidized soybean oil (ESO). The results showed that soybean oil based polyol ester could improve the thermal stability. More relative content of ester bonds connected to the structure of soybean oil polyol ester and ester bonds with higher thermal stability limited the decomposition of those segments with lower-thermal-stability chain segments. DMA results and mechanical data illustrated that the plasticizing effect of SOPE-2 and ESOPE-2 on PVC is better than that of DOP, ESO, SOPE-1 and ESOPE-1. Plasticizing effect of ECOPE-2 on PVC is more efficient than DOP. Migration stability tests showed that with the increasing of the molecular weight, branching degree of molecular and ester bands of soybean oil based polyol ester, the migration stability enhanced. The results showed that the derivative of a kind of renewable natural vegetable oil may be more environ-

mentally friendly than DOP and other petroleum-based plasticizers.

ACKNOWLEDGEMENTS

This work was supported by National 12th Five-year Science and Technology Support Plan (Grant No. 2015BAD15B08); Jiangsu Province Natural Science Foundation of China (Grant No. BK20141074).

REFERENCES

1. M. A. D. Silva, M. G. A. Vieira, A. C. G. Maçumoto and M. M. Beppu, *Polym. Test.*, **30**, 478 (2011).
2. L. Annika and H. Minna, *J. Appl. Polym. Sci.*, **104**, 2458 (2007).
3. C. E. Mackintosh, J. A. Maldonado, M. G. Ikononou and F. A. P. C. Gobas, *Environ. Sci. Technol.*, **40**, 3481 (2006).
4. P. A. Clausen, V. Hansen, L. Gunnarsen, A. Afshari and P. Wolkoff, *Environ. Sci. Technol.*, **38**, 2531 (2004).
5. N. R. Janjua, G. K. Mortensen, A. M. Andersson, B. Kongshoj, J. A. Tickner, T. Schettler, T. Guidotti, M. McCally and M. Rossi, *J. Ind. Med.*, **39**, 100 (2001).
6. T. Sun and R. Thom, *J. Elastom. Plast.*, **42**(2), 129 (2010).
7. P. K. Gamage and A. S. Farid, *J. Appl. Polym. Sci.*, **121**, 823 (2011).
8. O. Fenollar, D. Garcia-Sanoguera, L. Sa'nchez-Na'cher, J. Lo'pez and R. Balart, *J. Appl. Polym. Sci.*, **124**, 2550 (2012).
9. C. Bueno-Ferrer, M. C. Garrigós and A. Jiménez, *Polymer Degrad. Stab.*, **95**, 2207 (2012).
10. P. Karmalm, T. Hjertberg, A. Jansson and R. Dahl, *Polymer Degrad. Stab.*, **94**, 2275 (2009).
11. K. Subbarao, S. Lucas, G. Michael, W. Benjamin and K. Dharma, *J. Vinyl. Addit. Technol.*, DOI:10.1002/vnl.21486
12. M. Bhakti, K. Mukesh and S. Anagha, *J. Appl. Polym. Sci.*, **32**, 17 (2015).
13. A. O. Pedro, M. L. G. Jerome, W. G. Gaele, H. W. Cesar, G. E. Sergio and B. Otavio, *J. Appl. Polym. Sci.* (2015), DOI:10.1002/APP42102.
14. A. Jean-Luc, L. Loic and C. Yves-Marie, *J. Appl. Polym. Sci.* (2014), DOI:10.1002/APP39983.
15. P. Karmalm, T. Hjertberg, A. Jansson, R. Dahl and K. Ankner, *Polymer Degrad. Stab.*, **94**, 1986 (2009).
16. B. Sun, B. I. Chaudhary, C. Shen, D. Mao, D. Yuan, G. Dai, B. Li and J. M. Cogen, *Polym. Eng. Sci.*, **53**, 1645 (2013).
17. B. I. Chaudhary, S. Wills and M. Mundra, US Patent, 8,859,654 B2 (2014).
18. J. Puyou, B. Caiying, H. Lihong and Z. Yonghong, *Korean J. Chem. Eng.*, **32**, 547 (2015).
19. F. Guodong, J. Puyou, Z. Liqiang, H. Lihong, Z. Meng and Z. Yonghong, *Korean J. Chem. Eng.*, **32**, 1201 (2015).
20. J. Puyou, Z. Meng H. Lihong, B. Caiying and Z. Yong-Hong, *J. Therm. Anal. Calorim.*, **120**, 1731 (2015).
21. J. Puyou, Z. Meng, L. Chengguo, Hu. Lihong, F. Guodong, B. Caiying and Z. Yonghong, *RSC Adv.*, **5**, 41169 (2015).
22. J. Puyou, Z. Meng, L. Chengguo, Hu. Lihong and Z. Yonghong, *J. Appl. Polym. Sci.* (2015), DOI:10.1002/APP42111.
23. Z. Liqiang, Z. Meng, Z. Yonghong and H. Lihong, *Polym. Degrad. Stab.*, **98**, 2784 (2013).
24. Z. Meng, P. Hui, Z. Liqiang, H. Lihong and Z. Yonghong, *Ind. Crop.*

- Prod.*, **59**, 135 (2014).
25. Z. Liqiang, Z. Meng, Hu. Lihong and Z. Yonghong, *Ind. Crop. Prod.*, **52**, 380 (2014).
26. L. Annika and H. Minna, *J. Appl. Polym. Sci.*, **100**, 2180 (2006).
27. A. F. Faria-Machado, M. A. D. Silva, M. G. A. Vieira and M. M. Beppu, *J. Appl. Polym. Sci.*, **27**, 3543 (2013).
28. H. Lai, Z. Wang, P. Wu, B. I. Chaudhary, S. S. Sengupta, J. M. Cogen and B. Li, *Ind. Eng. Chem. Res.*, **51**, 9365, 28 (2012).
29. G. N. Pratiksha, T. M. Shashank and V. S. Vikrant, *Iran Polym. J.*, **23**, 599 (2014).
30. O. Fenollar, D. Garcia-Sanoguera, L. Sanchez-Nacher, J. Lopez and R. Balart, *J. Mater. Sci.*, **45**, 4406 (2010).
31. J. L. Audic, D. Reyx and J. C. Brosse, *J. Appl. Polym. Sci.*, **89**, 1291 (2003).
32. Y. Baohong, B. Yongping and C. Yingjie, *J. Appl. Polym. Sci.*, **115**, 2178 (2010).
33. O. Yuanhui, D. Xuejia and Z. Long, *J. Appl. Polym. Sci.* (2014), DOI: 10.1002/APP.39763.
34. L. Chengguo, L. Jun, L. Wen and Z. Yonghong, *Ind. Crop. Prod.*, **52**, 329 (2014).
35. T. Sun and R. Thom, *J. Elastom. Plast.*, **42**, 129 (2010).
36. Q. Yao and C. A. Wilkie, *J. Vinyl. Addit. Technol.*, **7**, 26 (2001).
37. Y. Soudais, L. Moga, J. Blazek and F. Lemort, *J. Anal. Appl. Pyrolysis*, **78**, 45 (2007).
38. Y. Li, C. Wang, G. Wang and Z. Qu, *J. Wuhan Univ. Technol.*, **2**, 101 (2008).
39. P. Vickraman and S. Ramamurthy, *Mater. Lett.*, **60**, 3431 (2006).
40. S. Ramesh, G. B. Teh, R. F. Louh, Y. K. Hou, P. Y. Sin and L. G. Yi, *Sadhana*, **35**, 87 (2010).