

Properties of poly(vinyl chloride) incorporated with a novel soybean oil based secondary plasticizer containing a flame retardant group

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ABSTRACT: A novel bio-based plasticizer containing flame retardant groups based on soybean oil (SOPE) was synthesized from epoxidized soybean oil (ESO) and diethyl phosphate through a ring-opening reaction. PVC blends plasticized with ESO and SOPE were prepared, respectively. Properties including rheological behavior, thermal stability, flame retardant performance, mechanical properties of PVC plasticized with ESO and SOPE were carefully studied. The results showed that the plasticized PVC blends indicated better compatibility, thermal, and mechanical properties. As a novel bio-based plasticizer containing flame retardant groups, the TGA data indicated that the thermal degradation temperature of PVC blends plasticized with SOPE could reach to 275.5°C. LOI tests and SEM indicated that the LOI value of PVC blends could increase from 24.2 to 33.6%, the flame retardant performance of SOPE was put into effect by promoting polymer carbonization and forming a consolidated and thick flame retardant coating quickly, which is effective to prohibit the heat flux and air incursion. The enhancement in flame retardancy will expand the application range of PVC materials plasticized with SOPE. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42111.

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INTRODUCTION

Poly(vinyl chloride) (PVC) is the second largest manufactured resin in the world.¹ PVC products are widely used in a large range of application such as window frames, wallpapers, pipes, flooring, cables, bottles, packaging and credit cards, audio records, medical tubing, blood bags, and children toys.² PVC is one of the clearest and toughest plastics, but it is also difficult to process due to its high melt viscosity caused by the rigid chain structure, which resulted in a relatively high processing temperature and high screw torque.³ Common resolution of the problem is to add inert plasticizers, which tend to impair the mechanical and thermal properties of the final product.⁴ The primary role of plasticizers is to improve the flexibility and process ability of PVC by lowering the second order transition temperature, the transition temperature (T_g).⁵ The Council of the IUPAC (International Union of Pure and Applied Chemistry) defined a plasticizer as “a substance or material incorporated in a material to increase its flexibility, workability, or distensibility.” Phthalates as the main plasticizer additives of PVC have been used around the world for years due to excellent plasticizing effect, but phthalates may migrate from PVC prod-

ucts to environments when the materials contact with biological fluids, which will take potential risks to human health when they are used in food packing, automotive products, insect repellents, blood storage bags, and medical devices.^{6–9} And the raw materials of phthalate are petroleum, scarcity of petroleum resources and the rising cost of petroleum products have led to the increasing trend towards developing of alternate sources of materials for industrial uses.

Recently, there has been a growing interesting in the use of plasticizers obtained from renewable resources because advantages of non-toxic, environmental, biodegradable, and renewable raw materials. A series of recent publications reported the synthesis and possible application of PVC plasticizers derived from renewable resources such as epoxidized sunflower oil,¹⁰ epoxidized safflower oil,¹¹ low-molecular-weight glycerol esters,¹² oleic acid polyester,¹³ rice fatty acid,¹ and epoxidized soybean oil (ESO).^{14,15} ESO has been used as plasticizer of PVC for years, but the synthesis of soybean oil (SO) including flame retardant groups and the mechanism of flame retardant has never been reported. In this study, we look forward to preparing a novel bio-based plasticizer containing retardant groups

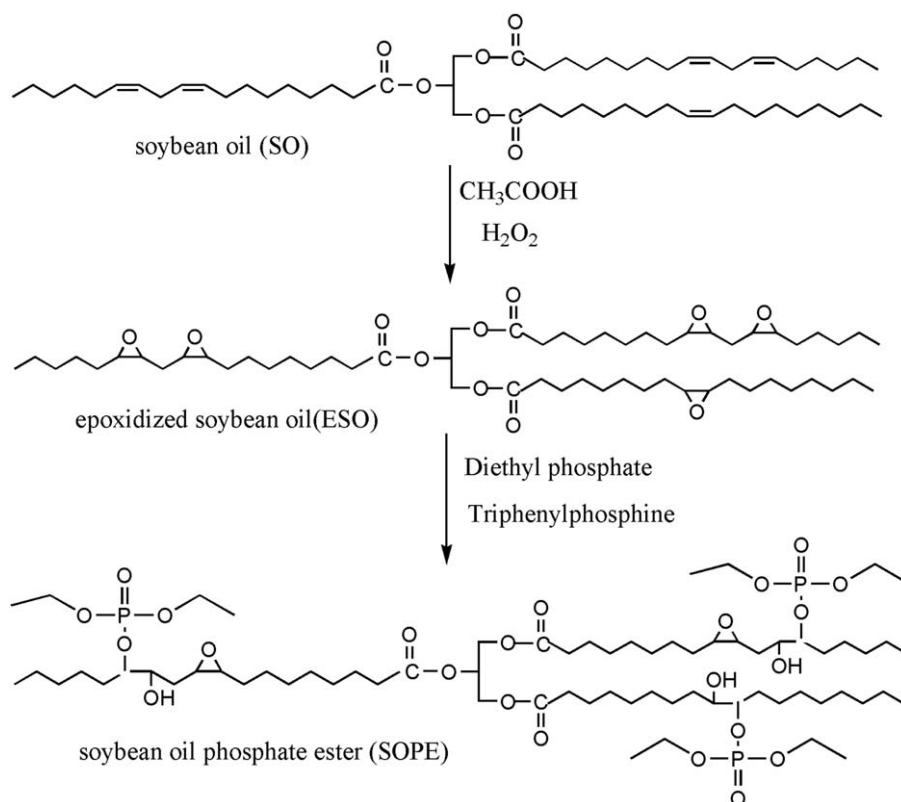


Figure 1. The idealized reaction scheme for the synthesis of ESO and SOPE.

based on SO, and partly to replace the phthalate as plasticizer of PVC.

In our present work, ESO was synthesized from SO, glacial acetic acid, phosphate, and hydrogen peroxide (H₂O₂). Then ESO was first time to convert to flame-retardant SOPE by reaction with diethyl phosphate using triphenylphosphine as catalyst. The structure and composition of ESO and SOPE were characterized by FTIR and ¹H NMR. PVC blends were prepared using ESO and SOPE as plasticizer, respectively. The interaction between PVC and plasticizer was studied and the degradation and fire retardant mechanism of PVC blends was analyzed.

EXPERIMENTAL

Materials

SO was provided by Arowana Group, China and was used without further purification. Phosphate, anhydrous acetic acid, phosphorus pentoxide, triethyl phosphate, and triphenylphosphine were obtained from Nanjing Chemical Reagent. Sodium hydroxide, hydrogen peroxide, methylbenzene were supplied by Aladdin Chemical. PVC was supplied by Hanwha (South Korea) with *K*-value 65.0 and degree of polymerization 1300 ± 100.

Synthesis of ESO

Hundred grams of SO, 10 g glacial acetic acid, and 0.5 g concentrated sulfuric acid were mixed in a four-necked round-bottom flask, which was equipped with a mechanical stirrer, condenser pipe, thermometer, and constant pressure funnel. Sixty milliliter hydrogen peroxide solution were dropped in the reaction in 30 min and stirred at 60°C for 8 h to complete

epoxidation reaction. Then the reaction mixture was separated from water with separating funnel and washed 3 times with distilled water, then removed the water with a rotary evaporator at 60°C. The chemical reaction process of ESO was shown in Figure 1.

Synthesis of Diethyl Phosphate

Ninety-one gram of triethyl phosphate were placed in a three-necked round-bottom flask equipped with a thermometer, a mechanical stirrer, and a condenser tube, 56.4 g phosphorus pentoxide were mixed in the three-necked round-bottom flask under 50°C in 2 h. Then 33.6 g ethyl alcohols absolute were dropped in the obtained polyphosphate intermediate and stirred at 100–110°C for 16 h to complete the reaction.

Table I. Composition of PVC Blend Plasticized with ESO and SOPE

Samples	PVC (g)	DOP (g)	ESO (g)	SOPE (g)	Thermal stabilizers (g)
A	100	40	0	0	2
B	100	35	5	0	2
C	100	30	10	0	2
D	100	25	15	0	2
E	100	20	20	0	2
F	100	35	0	5	2
G	100	30	0	10	2
H	100	25	0	15	2
I	100	20	0	20	2

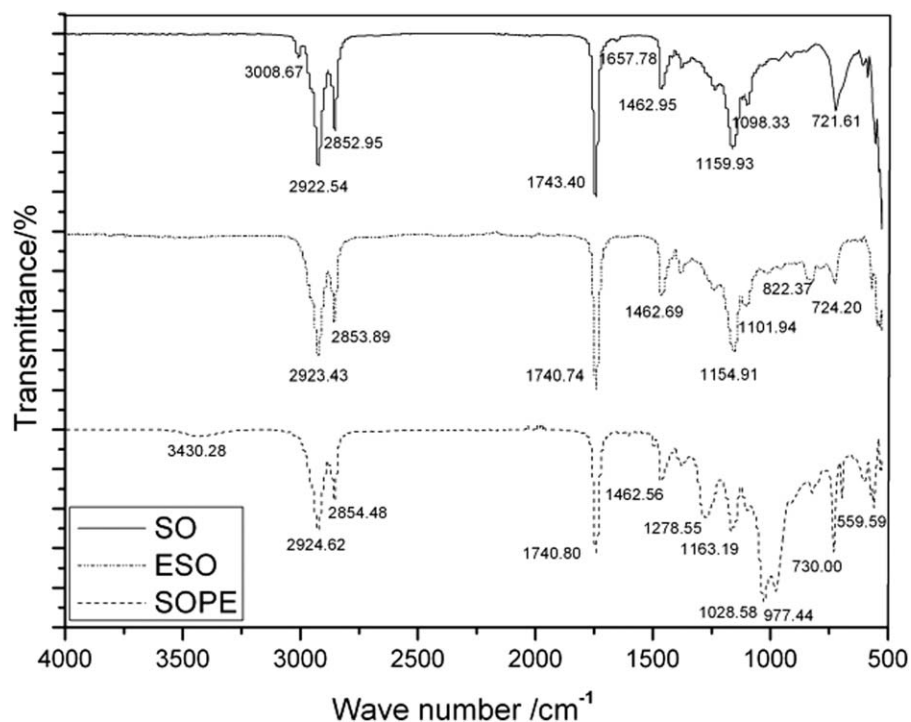


Figure 2. FTIR spectra of SO, ESO, and SOPE.

Synthesis of SOPE

Hundred grams of ESO and 80 g toluene were mixed in a three necked round-bottom flask equipped with a tetrafluoroethylene stirrer, a thermometer and a condenser pipe. The mixture of diethyl phosphate (30 g), toluene (80 g), and triphenylphosphine (0.1 g) were dropped in the reaction in 30 min at 40°C. The reaction proceeded with continuous stirring at 75°C for 4 h. Then the reaction mixture was cooled to room temperature and washed to pH = 7 with sodium hydroxide solution and washed 3 times with distilled water, then removed the water with rotary

evaporator at 60°C. Chemical reaction processes of SOPE were shown in Figure 1.

Preparation of Blends

PVC blends were melting process at 165°C for 5 min at 50 rpm using Poly Lab Torque rheometer (Hakke Instrument, Germany). The PVC was pretreated by drying at 60°C for 2 h to eliminate possible absorbed water on the surface of the particle. Formulations used for preparing plasticized PVC blends were shown in Table I. Dumbbell-shaped samples of blends were

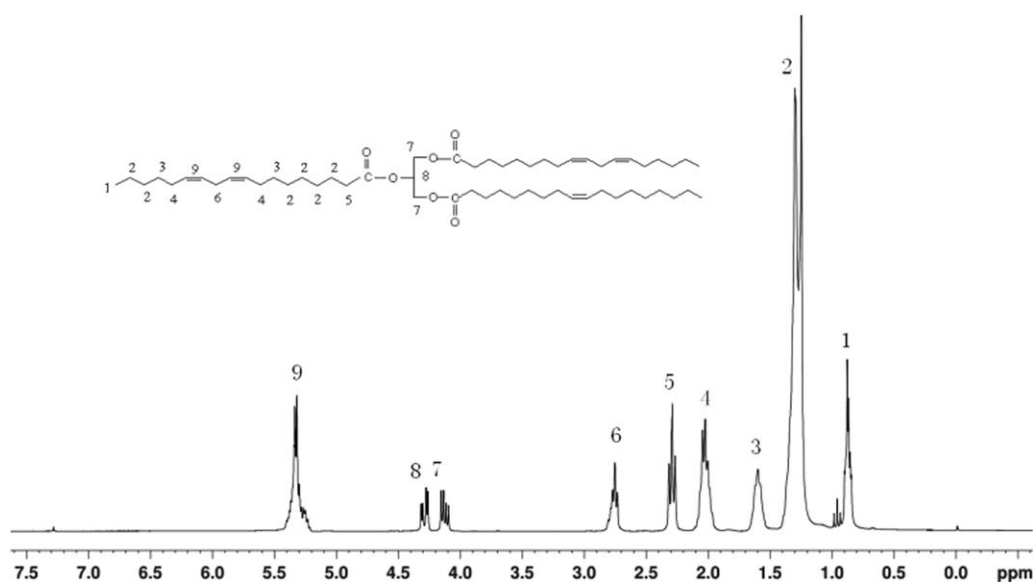


Figure 3. ¹H-NMR spectra of SO.

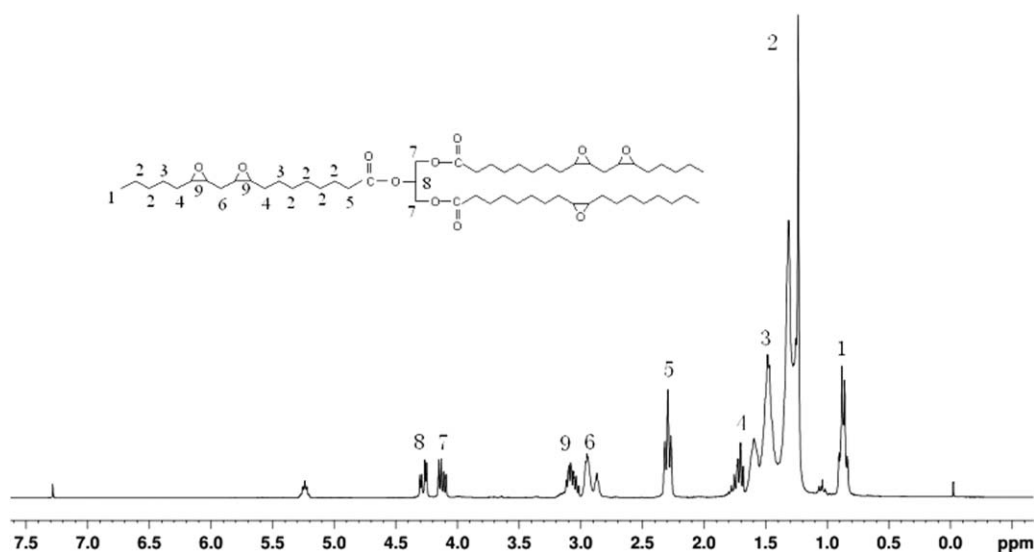


Figure 4. ^1H -NMR spectra of ESO.

molded on a MiniJetII Micro-injection molding machine (Hakke Instrument, Germany) according to GB/T 17037.1–1997(China). Moulding conditions were set at 165°C for 5 min at 550 Bar.

Characterization

FTIR. FTIR spectra were obtained on a Nicolet iS10 FTIR (Nicolet Instrument, US). The spectrum was acquired in the range of 4000 to 500 cm^{-1} at a resolution of 4 cm^{-1} .

^1H NMR. Nuclear magnetic resonance (NMR) spectra (^1H) were recorded using an AV-300 instrument (Bruker Instrument, Germany) with tetrametylsilane as an internal standard.

TGA. The thermal ability of PVC blends was characterized in a TG209F1 TGA thermal analysis instruments (Netzsch Instrument, Germany) in N_2 atmosphere (50 mL/min) at a heating

rate of 10°C/min. Five milligram samples were put into platinum pans and scanned from 30 to 600°C.

Flame Retardant Performance Analysis

Limiting oxygen index (LOI) tests were carried according to the standard of Plastics-Determination of burning behavior by oxygen index (GB/T 2406.1–2008, China) using JF-3 oxygen index measuring instrument (Nanjing Lei instrument, China), Size [80 mm (L) \times 10 mm (W) \times 4 mm (T)] of samples was prepared.

SEM

The surfaces of PVC blends and carbon layer were investigated with a Hitachi 3400-1 (Hitachi, Japan) scanning electron microscope instrument, operated at 12 kV. The fracture of all surfaces was sputtered with gold to avoid electrostatic charging during examination.

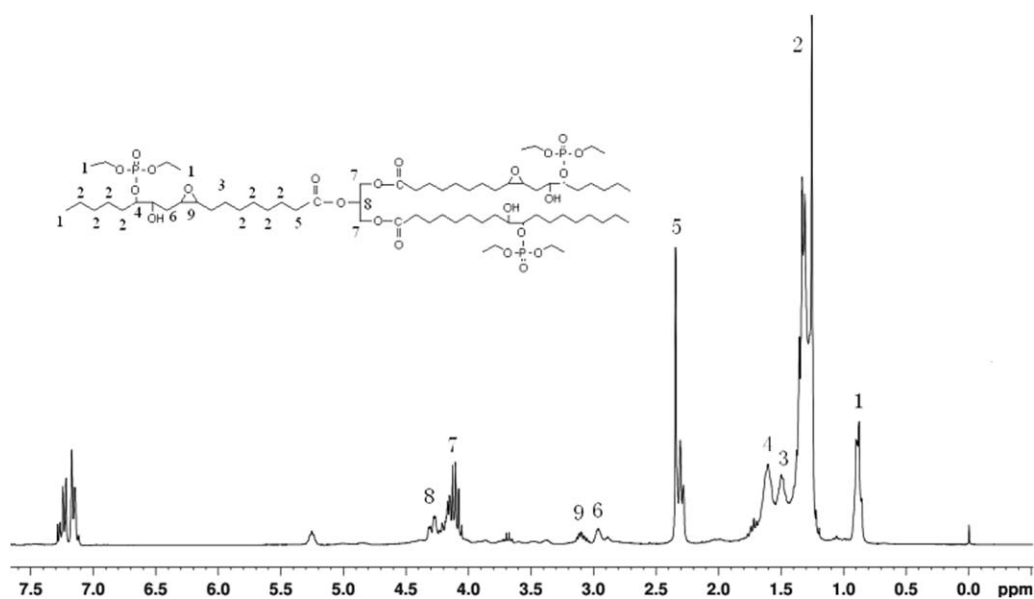


Figure 5. ^1H -NMR spectra of SOPE.

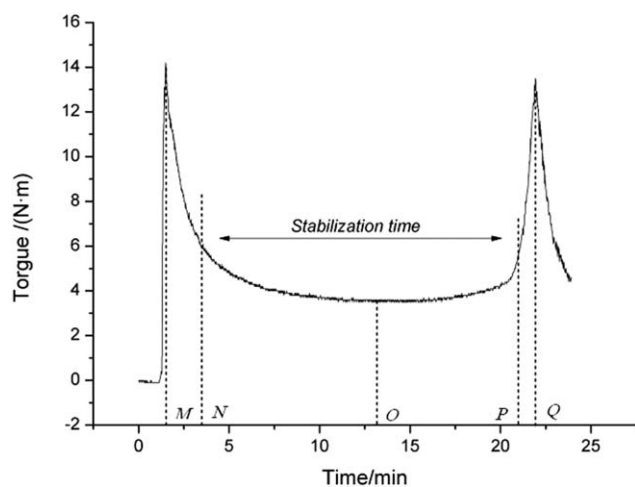


Figure 6. The torque rheological curve of PVC blend.

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

Tensile Properties

The property including tensile modulus, tensile strength, and elongation at break was determined according GB/T 1040.1–2006 (China) under ambient conditions, using E43.104 Universal Testing Machine (MTS Instrument, China). The reported values were the average of at least.

RESULTS AND DISCUSSION

FTIR

Structures of the plasticizers based on SO were monitored using FTIR. The spectra and the parameters were depicted in Figure 2. Several characteristic peaks were indicated in the spectrum of

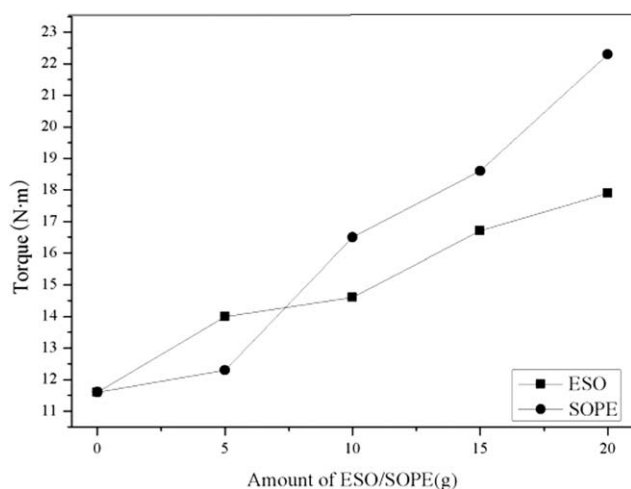


Figure 7. Torque variation during blends mixing in relation to the plasticizer content.

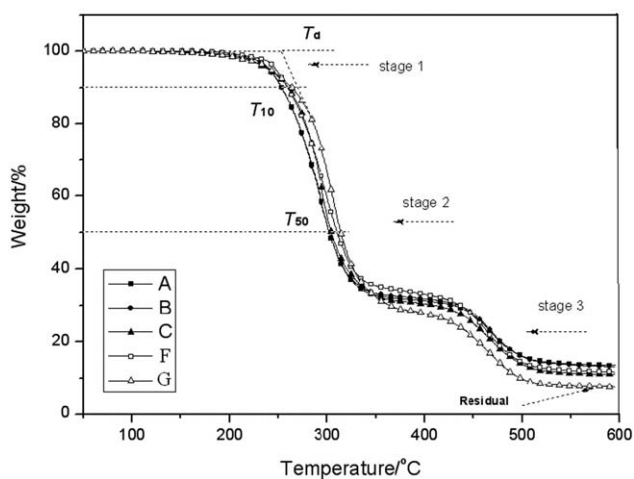


Figure 8. TG curves of PVC blends.

SO, the band at 3008.67 cm^{-1} , which is assigned to the absorption of $=\text{C}-\text{H}$ bonds, methyl and methylene groups (2922.54 and 2852.95 cm^{-1}), ester carbonyl groups (1743.40 cm^{-1}), and the band at 1657.78 cm^{-1} , which is assigned to the absorption of $-\text{C}=\text{C}-$ bonds. Comparing to the spectrum of ESO, the peaks of $=\text{C}-\text{H}$ groups and $-\text{C}=\text{C}-$ groups had disappeared, and the characteristic peak of $\text{C}-\text{O}-\text{C}$ vibration was observed around 822.37 cm^{-1} , implying that a complete epoxidation reaction had occurred.

The FTIR spectrum of SOPE was also presented in Figure 2. The characteristic peak of $\text{P}-\text{O}-\text{C}$ symmetric bending vibration had appeared at 1028.58 cm^{-1} comparing to the spectrum of ESO. The SOPE spectra showed that the intensity of the peak at 822.37 cm^{-1} decreased. Indicating some epoxy groups were expended in the formation of phosphate groups.

^1H NMR

The ^1H NMR spectra of SO, ESO, and SOPE products were shown in Figures 3–5, respectively. As indicated in the spectrum of SO (Figure 3), the peak at 0.8 ppm is corresponding to the terminal methyl protons of fatty acids ($-\text{CH}_3-$), the multi-peaks around 4.2–4.4 ppm are corresponding to the methylene

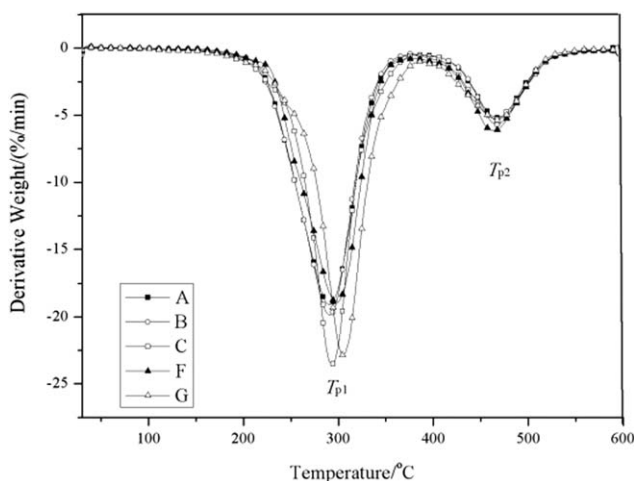


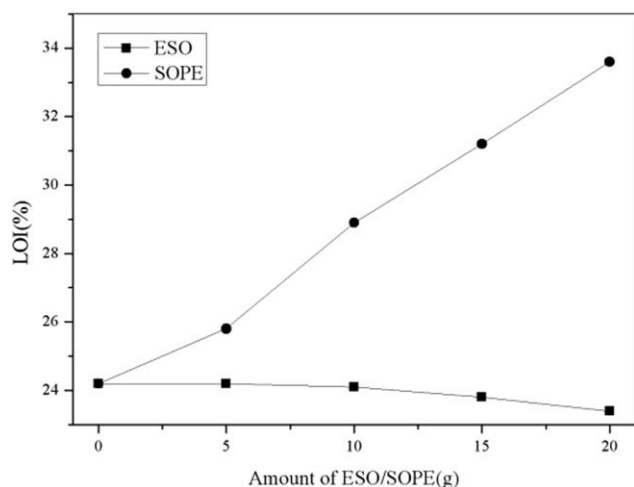
Figure 9. DTG curves of PVC blends.

Table II. The Parameters of TGA of PVC Blends

Samples	T_d (°C)	T_{10} (°C)	T_{50} (°C)	T_{P1} (°C)	T_{P2} (°C)	T_g (°C)	Residual (%)
A	249.4	258.1	283.2	278.9	457.3	27.5	17.02
B	253.6	257.8	304	292.5	468.3	34.2	13.11
C	265.9	278.6	306.1	294.9	468.8	43	10.96
F	258.8	262.6	310.2	299.5	465.3	46.5	12.12
G	275.7	264.2	319.1	306.7	469.1	49.8	7.51

protons of glycerol, 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.¹⁶ The peak at 5.3 ppm is corresponding to the double bond protons ($-\text{CH}=\text{CH}-$) of fatty acids. The fatty acid proton ($[-\text{CH}_2-\text{CO}]$) were in the range of 2.3 ppm and the range of 1.35 ppm was contributed to the other methylene protons. The Figure 4 depicted the ^1H NMR spectra of ESO, as the epoxidation reaction of SO processed, the protons signals in the 5.3 ppm region of the spectrum of SO associated with the $-\text{CH}=\text{CH}-$ bonds were replaced in the spectrum of ESO by multiplets around 3.1–3.2 ppm corresponding to protons on the epoxy groups. In addition, the peak of $-\text{C}=\text{C}-$ protons around 5.3 ppm in the spectrum of ESO had disappeared, all of the data implied that the $-\text{CH}=\text{CH}-$ bonds of SO were reacted with H_2O_2 .

The ^1H NMR spectra of SOPE products are shown in Figure 5. Comparing to the ^1H NMR spectra of ESO, the region 1.6 ppm is associated with the $-\text{P}-\text{O}-\text{CH}-$ at the middle of the SOPE while there are multiplets in the range of 3.1–3.2 ppm shown in the Figure 4, which belong to the epoxy groups. The signal at 4.2–4.4 ppm may be shifted in the ESO spectrum owing to the presence of the epoxy groups, and was broadened indicating that ring opening may have occurred following epoxidation with diethyl phosphate.^{17,18} Compared to the ^1H NMR of SO, ESO, and SOPE, we can conclude that the ESO and SOPE were prepared.

**Figure 10.** LOI variation in relation to plasticizer content.

Blend Mixtures and Torque Evaluation

To verify the melting behavior, processing data were collected during mixing in the Haake chamber. The three important variables in this process are the chamber temperature, rotating speed, and rotor torque. The chamber temperature and rotating speed was fixed, and the torque data were collected and related directly to the melt viscosity, the material resistance to flow. During processing, the melt temperature remained approximately constant. The torque rheological curve of PVC blends and the figure of torque values relative to the proportion of plasticizer in blends were shown in Figures 6 and 7. Seen from the Figure 6, the point M is the feeding peak, which indicates the maximum torque, the point N, O, P, and Q is plasticizing peak, minimum torque, starting point of degradation, and end of degradation, respectively. PVC material should be taken from torque rheometer and the thermoplastic processing should be stopped at the point of stable torque. PVC will be started degrading after the time.

Figure 7 presents the torque values relative to the proportion of plasticizer in PVC blends for the processing time of 5 min. With the increasing of ESO and SOPE, the torque of PVC blends increased from 11.6 N·m (A) to 17.9 N·m (C), and 22.3 N·m (I). The torque increment could increase the melt viscosity and would be not conducive to thermoplastic processing of PVC blends. Three-dimensional structure of the long-chain of ESO and SOPE may cause torque increment of PVC blends.

TGA

The thermal degradation of PVC plasticized with ESO and SOPE was studied by TGA. The curves of TGA and DTA were depicted in Figures 8 and 9 respectively. Table II summarized the parameters of TGA and DTA of PVC blends. From TGA curves in Figure 8, all of the PVC blends were thermally stable in N_2 atmosphere below 90°C and divided into a three-stage thermal degradation process above the temperature. The first stage degradation at around 90–250°C could be attributed to evaporation of water and small molecules. The second stage at around 250–440°C is the fastest and is corresponding to the formation and stoichiometric elimination of HCl. The last stage at above 440°C is attributed to cross linking containing $\text{C}=\text{C}$ bonds. Thermal degradation of polyenes involves cyclization and splitting of chains.^{1,4,5} In addition, the slope of TGA curves of A is bigger than the others; it indicated that A is worst in thermal stability, and the thermal stability of E is the best of all the samples. DTA curves of PVC blends showed two degradation peaks at around 290 and 460°C, and PVC blends

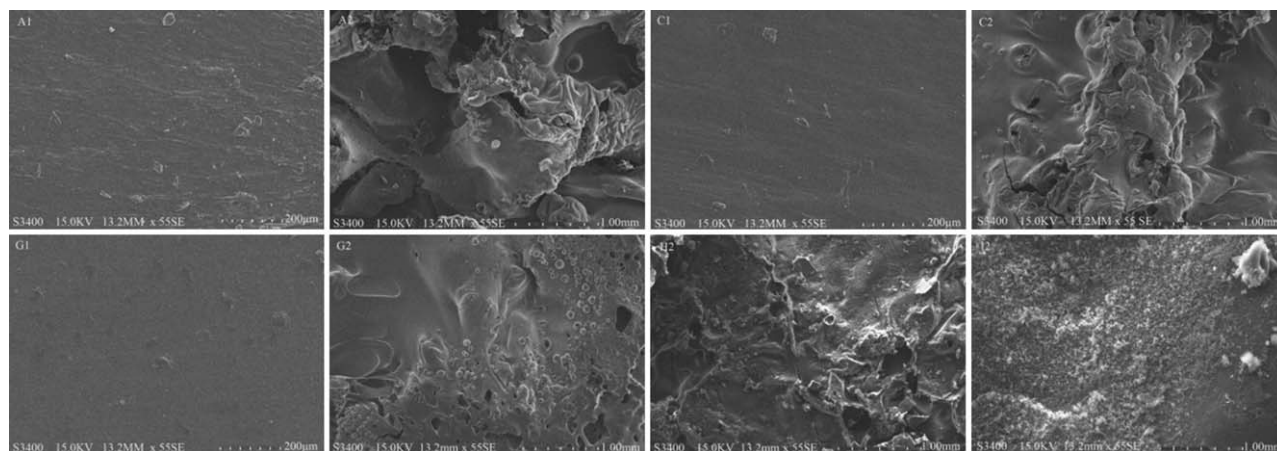


Figure 11. SEM micrographs of surfaces of PVC blend (A1), (C1), (G1), (A2), (C2), (G2), (H2), (I2).

plasticized with ESO and SOPE showed similar behavior with two mass loss peaks. The two mass peaks are corresponding to two faster thermal degradation stages.

Table II summarized the thermal properties data of these PVC blends, including decomposition temperature (T_d), 10% and 50% weight-loss temperature (T_{10} and T_{50}) and temperature at the maximum weight-loss temperature rate (T_p). As the increase of content of ESO and SOPE, T_{10} , T_d , and T_p increased. The samples of F and G increased obviously. Because the diethyl phosphate had degraded and phosphinic acid was generated with the temperature increasing. Phosphinic acid make PVC dechlorination to produce carbonization zone and O_2 and heat were prevented, which make PVC blend thermal stability.

Flame Retardant Performance Analysis

The combustion performance of PVC blends has been evaluated by the LOI tests. LOI tests were conducted and the LOI variation in relation to plasticizer content was depicted in Figure 10. From the Figure 10, the LOI value decreased from 24.2% (A) to 23.4% (E) with the addition of 20 g ESO, and the LOI value increased from 24.2% (A) to 33.6% (I) with the addition of 20 g SOPE. Generally, materials exhibited (LOI) values greater than 26% will show self-extinguishing behaviors and considered to be good flamer retardant.^{19,20} Therefore, ESO could not be used as flame retardant plasticizer of PVC, while the increase of LOI value indicated that SOPE was an effectively flame retardant plasticizer for PVC.

The physical structure of the charring layer plays an important role in the performance of the flame retardant.²¹ SEM images of the residual char after Limit oxygen index test were shown in Figure 11, the marked number A2, C2, G2, H2, and I2 are corresponding to sample A, C, G, H, and I, respectively. With the increment of ESO and SOPE, surface morphology of residual char is different obviously comparing to each other. Char surface of A and C is separated by a net of cracks. The width of cracks is about 200 μm , and a large number of irregular micro hubble structure distributed on the surface of char residue. The incomplete char coat cannot effectively prohibit heat flux and air incursion penetrating the underlying heat polymer. Therefore, ESO could not play any role in the performance of the

flame retardant. On the contrary, I2 shows that the char surface of sample I is continuous and compact, and any crack could not be observed, indicating strong adhesive between the SOPE and the PVC matrix. There were some P—O and P—C bonds existed in the structure of SOPE, which makes it still thermal stability under 350°C. The existence of diethyl phosphate grafting in the SO phosphate molecular chain, when it was burned, diethyl phosphate degraded and phosphinic acid was generated. Metaphosphate and poly metaphosphate would be generated after dehydration of phosphinic acid. Metaphosphate and poly metaphosphate could promote polymer carbonization and form a consolidated and thick flame retardant coating quickly. From the I2, it can be seen that char layer of the flame retardant coating is consolidated and thick, which is effectively to prohibit the degradation products penetrating the underlying heated polymer. The good dispersion and compatibility of SOPE and PVC matrix play an important role in the performance of the flame retardant.

SEM

The properties of particle filled composites strongly depend on the dispersion and compatibility of fillers in polymer matrix.^{21,22} The SEM images of the surface of PVC plasticized with ESO and SOPE are shown in Figure 11, the marked number A1, C1, and G1 are corresponding to sample A, C, and G, respectively. From the A1, many particles and fractures could be observed on the external surface of A. The particles appearing on the surface are properly the result of some plasticizer excess that is scattered outside the PVC matrix. It caused the eventual migration of plasticizer out of PVC during processing and using. While PVC plasticized with ESO and SOPE showed homogeneous and smooth surface as observed in C1 and G1. ESO and SOPE disperse in the PVC matrix uniformly and surrounded intimately with PVC continuous phase, and there is not a clear boundary between them to be observed. So there are good interfacial adhesion and plasticizer between ESO, SOPE, and PVC.

DMA

DMA technology was employed to investigate the glass transition temperature (T_g) of the PVC blends, the results were showed in Figure 12 and Table III. It was observed that there

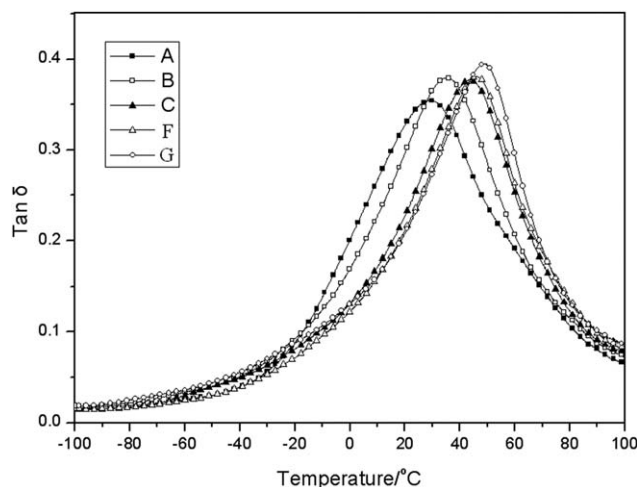


Figure 12. DMA curves of PVC blends.

was only a $\tan \delta$ peak existed in every DMA curve, which indicated that compatibility of the PVC and two kinds of functional plasticizers is excellent, and the DMA data indicated that the $\tan \delta$ peak shift to higher temperature with the increasing content of ESO and SOPE. From the Table III, the T_g increased from 27.5 to 43°C with the content of ESO increased from 0 to 10 g in PVC blend, and the T_g increased from 27.5 to 49.8°C with the content of SOPE increased from 0 to 10 g in PVC blend. The reason might be that the applied force between epoxy bonds or phosphate bonds and molecular chain of PVC become strong, and the motion of the molecular chain of PVC was decreased.

Tensile Properties

Plasticizer plays an important role in the mechanical properties of PVC blends. Hence, tensile strength along with elongation at break is a good effective way to evaluate the efficiency of plasticizers. Table III summarized the values of the mechanical properties of PVC blends. A significant influence of the addition of different content ESO and SOPE for PVC blends could be observed. With addition of 5–10 g ESO and SOPE and reduction of DOP in the PVC blends, it caused a significant decrease of ~50% and 70% in elongation at break but tensile strength

Table III. The Detail Mechanical Properties of PVC Blends

Samples	Tensile strength (Mpa)	Elongation at break (%)	Modulus of elasticity (Mpa)
A	16.32	350.12	6.8
B	16.58	241.59	14.13
C	16.71	165.79	103.89
D	17.23	126.59	189.74
E	18.36	98.36	212.3
F	16.36	169.51	13.15
G	16.60	93.18	76
H	18.98	46.30	102.12
I	22.30	8.11	127.01

changed a little. But it is not accordance with the common rule that the plasticizer can increase the elongation at break and decrease the tensile strength Modulus of elasticity. It could illustrate that the ESO and SOPE have plasticization in PVC but the plasticizing efficiency is lower than DOP. The results could be explained that both ESO and SOPE molecular have less electron atmosphere than DOP molecular, and the interaction between them and PVC molecular is weaker than DOP molecule. However, the appropriate PVC products could be prepared by modifying the composition of PVC blends.

CONCLUSIONS

In this work, ESO and SOPE were synthesized successfully by using SO. The PVC blends were prepared and the ESO and SOPE were as auxiliary plasticizer, respectively. Thermal degradation data of PVC plasticized with ESO and SOPE showed that the T_d of PVC blends increased from 249.4 to 265.9°C and 275.7°C, the T_g increased from 27.5 to 43°C and 49.8°C, respectively. It indicated that both of plasticizers could improve the thermal ability of PVC blends. With the increase of content of SOPE in the PVC blends, T_{10} , T_{db} and T_p of D and G sample increased obviously, because the diethyl phosphate had degraded and phosphinic acid was generated with the temperature increasing. Phosphinic acid makes PVC dechlorination to produce carbonization zone and O_2 and heat were prevented, which makes PVC blend thermally stable. LOI tests showed that the LOI value of PVC blends could increase from 24.2% to 33.6%, the flame retardant performance of SOPE was put into effect by promoting polymer carbonization and forming a consolidated and thick flame retardant coating quickly, which was effective to prohibit the heat flux and air incursion. The SEM and torque data indicated that both plasticizers increased the melt viscosity in the melting process and improve the compatibility, which had a good interracial adhesion and plasticization with PVC. All results demonstrated that SOPE could partially substitute phthalates as the functionally plasticizer of PVC.

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