

Preparation and Application of Epoxy Oil-Based Fire-Retardant Plasticizer for PVC

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An epoxy oil-based fire-retardant plasticizer with a triazine ring structure (THEIC-SBOE) has been prepared by transesterification and epoxidation using *tris*(2-hydroxyethyl)isocyanurate and soybean oil methyl ester as the main raw materials. The structure of THEIC-SBOE has been characterized by FTIR, ¹H NMR and ¹³C NMR spectroscopies and elemental analysis and its thermal stability has been measured by thermogravimetric analysis. Its epoxy value and acid value have been determined as 4.3 % and 0.6 mg KOH g⁻¹, respectively. Examination of the morphology of carbon residue from PVC by scanning electron microscopy showed THEIC-SBOE to serve as an intumescent flame retardant. The results showed that, with the same plasticizer contents incorporated into PVC, THEIC-SBOE imparted similar mechanical properties as epoxidized soybean oil. Furthermore, PVC blends incorporating the synthesized plasticizer THEIC-SBOE displayed better fire-retardant properties than those incorporating dioctyl phthalate. The limiting oxygen index of such a PVC blend reached 28.4 % with 35 % (w/w) THEIC-SBOE incorporation.

Keywords: Epoxy oil-based, Fire-retardant, Plasticizer, Poly(vinyl chloride), Limiting oxygen index.

INTRODUCTION

Among the many additives incorporated into polymers that serve to improve certain properties, plasticizers account for a large fraction, as they can constitute up to 40 % of the overall material^{1,2}. Approximately 80 % of all plasticizers produced worldwide are used in poly(vinyl chloride) (PVC) formulations and about 90 % of the plasticizers used for PVC are diesters of phthalic acid^{3,4}. In recent years, vegetable oil modification technology (*e.g.*, the production of epoxidized oil, biodiesel synthesis, among others) has attracted the interest of manufacturers and researchers since these products are obtained from natural renewable sources and can be used as raw materials in chemical industries^{5,6}. Epoxidized soybean oil (ESO) and other epoxidized vegetable oils are extensively used in industry as stabilizers and plasticizers in PVC matrices^{7,8}.

However, when such plasticizers (*e.g.*, dioctyl phthalate, epoxidized soybean oil) are added to PVC, which has a high chlorine content and therefore inherent flame retardancy, the product can be rendered highly flammable. Hence, there is a need for more fire-retardant plasticizers. Epoxy oil-based fire-retardant plasticizers based on natural raw materials would be renewable and biodegradable. This is in line with the development trend of modern environmental and ecological security. *tris*(2-Hydroxyethyl)isocyanurate (THEIC) containing a

triazine ring structure shows excellent chemical stability and flame retardancy. In addition, it has three reactive hydroxyethyl groups connected to the stable triazine ring⁹⁻¹¹. In this work, we describe the preparation of an epoxy oil-based fire-retardant plasticizer. First, THEIC-soybean oil ester was synthesized by transesterification between THEIC and soybean oil methyl ester using tetrabutyl titanate as a catalyst. Second, THEIC-SBOE was generated by reacting the double bonds in THEIC-soybean oil ester with formic acid generated *in situ*. The structure of THEIC-SBOE was characterized by FTIR, ¹H NMR and ¹³C NMR spectroscopies and by elemental analysis and its thermal stability was measured by thermogravimetric analysis (TGA). Poly(vinyl chloride) composites plasticized by the synthesized THEIC-SBOE were then tested to examine their mechanical properties, such as tensile strength and elongation at break and their flame retardation as quantified by limiting oxygen index.

EXPERIMENTAL

Soybean oil methyl ester, 35 % hydrogen peroxide, *p*-toluenesulfonic acid (PTSA) and tetrabutyl titanate were supplied by Jiangsu Qianglin Bio-Energy & Bio-Materials Co., Ltd. (Chanzhou, China; industrial grade); formic acid, methanol, sodium hydroxide and *tris*(2-hydroxyethyl)isocyanurate

were purchased from Shanghai Lingfeng Chemical Reagent Co. (Shanghai, China; AR). Poly(vinyl chloride) powder (SG-III), dioctyl phthalate, Sb_2O_3 and epoxidized soybean oil were provided by Jiangsu shang shang cable group (Changzhou, China; industrial grade).

Synthesis of flame-retardant plasticizer (THEIC-SBOE):

In the first step, THEIC, soybean oil methyl ester and tetrabutyl titanate were added to a three-necked flask equipped with a stirring device and a thorn fractionating column in a molar ratio of 1:4:0.01. Among these reagents, tetrabutyl titanate served as a catalyst. The transesterification reaction mixture was maintained at around 230 °C under stirring until no more methanol was distilled off. The excess soybean oil methyl ester was removed by distillation. The product was then dried to obtain THEIC-soybean oil ester. The transesterification reaction is illustrated in **Scheme-I**^{12,13}.

In the second step, THEIC-soybean oil ester (100 g) and formic acid (2 g) were placed in a three-necked flask equipped with a stirrer, a thermometer and a pressure-equalizing dropping funnel. *p*-Toluenesulfonic acid (3 g) was added as a catalyst and the mixture was stirred at 65–70 °C. Hydrogen peroxide (35 %, v/v; 20 g) was then slowly dropped into the reaction mixture at such a rate as to maintain the temperature at 65–70 °C until the epoxy value of the product showed no further change. The mixture was then slowly poured into a separatory funnel, the layers were allowed to separate and the lower aqueous phase was drained. The upper organic layer was then washed sequentially with 2 % sodium hydroxide solution and distilled water and then the water was distilled off under reduced pressure to afford the product epoxy oil-based fire-retardant plasticizer with a triazine ring structure (THEIC-SBOE)^{14,15}.

FTIR, NMR, TG and elemental analysis: The structure of THEIC-SBOE was characterized spectroscopically. Its IR spectrum was acquired on a Nicolet 5 FTIR-750 infrared spectrometer (Nicolet, U.S.A.) with a resolution of 4 cm^{-1} and a scanning range of 4000–400 cm^{-1} . Its ^1H and ^{13}C NMR spectra were recorded from a solution in CDCl_3 on an Avance AVII-400 NMR spectrometer (Bruker, Germany). The thermal stability of THEIC-SBOE was characterized by thermogravimetric analysis (TG, Netzsch 409PC, Germany). TG conditions: N_2 atmosphere, heating rate of 10 °C/min over the range 50–600 °C. Elemental analysis was performed with a PE-2400 elemental analyzer (PE Co., U.S.A.). Epoxy value was measured according to ASTM standard method D1652-04¹⁶. Hydroxyl number was determined according to ASTM D6342-2008¹⁷. Acid value was determined according to GB/T 1668-2008¹⁸.

Plasticization of PVC resin: The synthesized plasticizer THEIC-SBOE was incorporated into PVC in order to evaluate

its plasticizing performance compared with those of epoxidized soybean oil and dioctyl phthalate by analyzing mechanical properties. Poly(vinyl chloride) blends were prepared using a torque rheometer and a MiniJet II micro-injection molding machine (Haake Co., Germany).

Flame retardancy tests: The limiting oxygen indices of PVC blends incorporating the plasticizers were measured according to GB/T2406-2008¹⁹. THEIC-SBOE, dioctyl phthalate, Sb_2O_3 and PVC were incorporated in different proportions by means of the abovementioned torque rheometer and micro-injection machine. Test samples were of dimensions 80 mm \times 5 mm \times 3 mm. The limiting oxygen indices were measured with a JF-3 type oxygen index tester (Jiangning District of Nanjing Analytical Instrument Factory).

RESULTS AND DISCUSSION

^1H and ^{13}C NMR spectra: As shown in Fig. 1, the obtained ^1H NMR spectrum featured the expected peaks for the proposed structure of THEIC-SBOE. $\delta = 5.36$ (9 H, OCH), 4.21 (6 H, 3 \times CH_2), 4.14 (6 H, 3 \times CH_2), 0.87 (9 H, 3 \times CH_3), 1.23 ppm (56 H, 28 \times CH_2). The peak at $\delta = 5.36$ ppm confirmed the generation of an epoxy group. The peaks at $\delta = 4.21$ and 4.14 ppm indicated the branched chain structure of THEIC. Fig. 2 shows the ^{13}C NMR spectrum (75.5 MHz, CDCl_3) of THEIC-SBOE: $\delta = 173.2, 148.4, 129.5, 127.5, 76.1, 60.3, 50.8, 44.6, 41.5, 50.8, 44.6, 41.5, 33.5, 29.1, 28.5, 26.6, 25.0, 24.3, 22.1, 13.5$ ppm. The peak at $\delta = 173.2$ ppm can be ascribed to the carbon of an ester group. The peaks at $\delta = 148.4, 129.5$ and 127.5 ppm can be ascribed to the three carbonyl carbon atoms of THEIC. The remaining peaks can be attributed to the aliphatic chain, indicating that the triazine ring was incorporated into the molecular chain during the reaction.

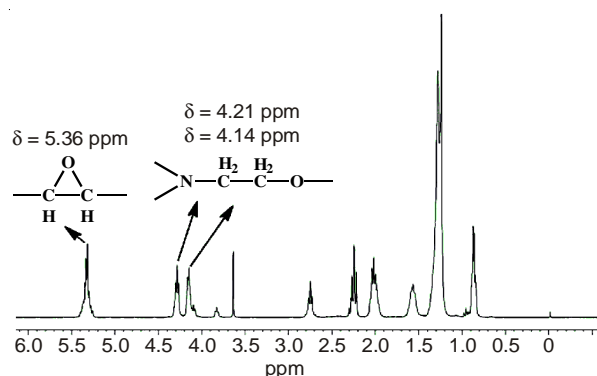
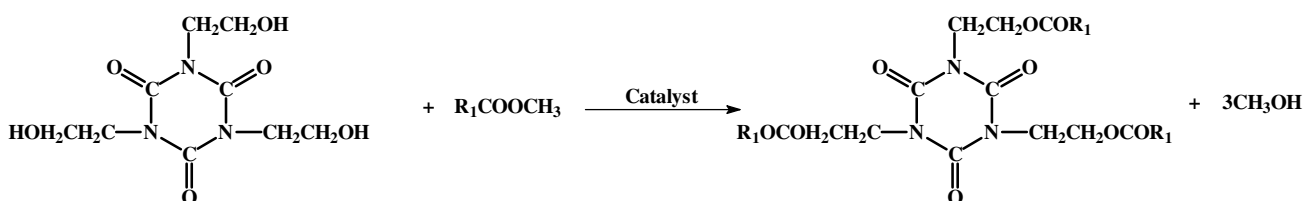


Fig. 1. ^1H NMR spectrum of THEIC-SBOE

FTIR spectra: Fig. 3 (a) and (b) show the FTIR spectra of THEIC-soybean oil ester and THEIC-SBOE, respectively. In



Scheme-I: Transesterification between THEIC and soybean oil methyl ester

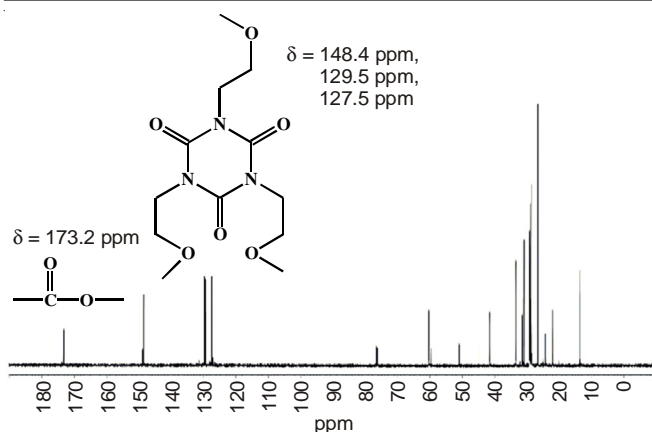
Fig. 2. ^{13}C NMR spectrum of THEIC-SBOE

Fig. 3 (a), the absorption peak at 1747 cm^{-1} can be ascribed to the carbonyl group on the aliphatic chain, that at 3017 cm^{-1} to the C-H stretching vibration of the unsaturated bond, those at 2918 and 2832 cm^{-1} to the C-H stretching vibration of the saturated hydrocarbon chain, those at 1462 and 1377 cm^{-1} to the methyl bending vibration and that at 1689 cm^{-1} to the C=O absorption of THEIC. This spectrum is consistent with successful transesterification between THEIC and soybean oil methyl ester.

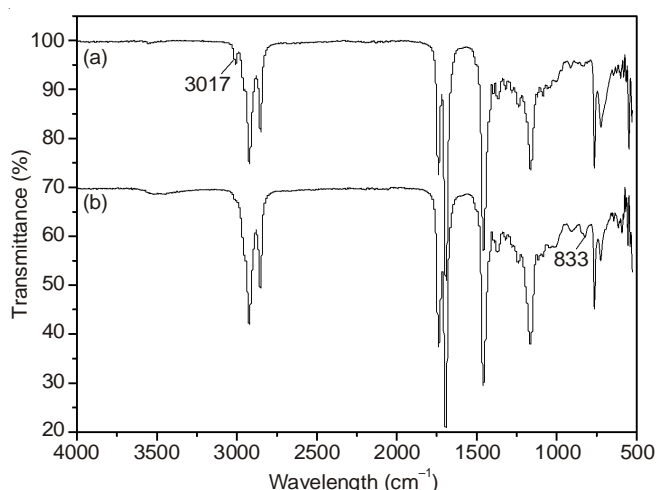


Fig. 3. IR spectra of THEIC-soybean oil ester (a) and THEIC-SBOE (b)

Comparing Fig. 3 (a) and (b), it is evident that the absorption at 3017 cm^{-1} observed for THEIC-soybean oil ester is no longer seen in the spectrum of THEIC-SBOE, whereas a new absorption peak appears at 833 cm^{-1} . That is to say, the characteristic absorption peak of =C-H in the ester is no longer seen in the spectrum of THEIC-SBOE and an epoxy bond absorption peak appears in the spectrum of this product. The results are consistent with conversion of C=C to an epoxy bond in the reaction.

The elemental composition can provide information about the different chemical structures and functional groups. The elemental compositions of THEIC, THEIC-soybean oil ester and THEIC-SBOE are shown in Table-1. On going from THEIC to THEIC-soybean oil ester, the composition changed from 41.22 % C, 6.10 % H, 16.03 % N, 36.64 % O to 69.79 % C, 10.15 % H, 4.20 % N, 15.85 % O. After the introduction of oxygen atoms by epoxidation, the C, H and N contents were slightly decreased and the O content increased from 15.85 to 19.35 %. These results further confirmed that THEIC-SBOE had been successfully synthesized.

Thermogravimetric analysis: Thermal stability is an important attribute of a plasticizer. As shown in Fig. 4, the thermal decomposition of THEIC-SBOE occurred in two steps. Firstly, the aliphatic chains and volatile components were lost; the later weight loss was related to the THEIC component, because the molecule contains a highly stable isocyanurate ring. For THEIC-SBOE, the temperatures corresponding to weight losses of 10, 50 and 90 % were 262, 419 and $454\text{ }^{\circ}\text{C}$, respectively. Thus, it can be seen that the product had excellent thermal stability, meeting the requirements of a plasticizer.

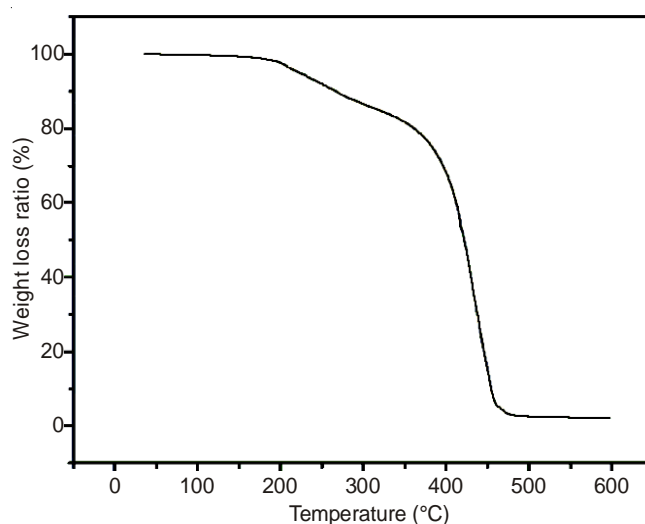


Fig. 4. Thermogravimetric analysis of THEIC-SBOE

Physical properties: The THEIC-SBOE product was obtained as a light-yellow liquid. Its acid value was 0.6 mg KOH g^{-1} , its hydroxyl value was $34.05\text{ mg KOH g}^{-1}$ and its epoxy value was 4.3 %.

Mechanical properties of the plasticizer: Specimens for tensile strength testing were prepared by mixing the raw materials according to the formulation in Table-2 using a torque rheometer and a micro-injection molding machine. Tensile strengths were measured according to GB/T 1040 1-2006²⁰. The tensile elongation rate was 5 mm/min and the test temperature was $25\text{ }^{\circ}\text{C}$.

TABLE-1
ELEMENTAL ANALYSIS OF *tris*(2-HYDROXYETHYL) ISOCYANURATE, THEIC-SOYBEAN OIL ESTER, AND THEIC-SBOE

	C (%)	H (%)	N (%)	O (%)
THEIC (calcd.)	41.22	6.10	16.03	36.64
THEIC-soybean oil ester	69.79	10.15	4.20	15.85
THEIC-SBOE (found)	67.67	9.92	3.04	19.35

TABLE-2
FORMULATION OF PVC PRODUCT

PVC (phr)	Plasticizer (phr)	Stabilizer (phr)
100	15	2

According to the data presented in Table-3, compared with the pure PVC sample, the tensile strength of THEIC-SBOE/PVC was reduced, which may be due to THEIC-SBOE increasing the distance and reducing the intermolecular forces between the PVC chains. However, the elongation at break was increased by 34.76 %, which may be due to van der Waals interaction between the plasticizer THEIC-SBOE and PVC polymer chains. On mixing the components at high temperature, THEIC-SBOE can be effectively inserted into the PVC molecular chain, increasing the mobility and improving elongation. When equal amounts of THEIC-SBOE and epoxidized soybean oil were incorporated into PVC, the tensile strength of the THEIC-SBOE/PVC resin was 21.75 MPa, 2.02 % lower than that with epoxidized soybean oil. The elongation at break was 55.19 %, similar to the 55.45 % seen for ESO/PVC, showing that THEIC-SBOE imparts PVC with superior mechanical properties.

TABLE-3
EFFECTS OF PLASTICIZER ON MECHANICAL PROPERTIES

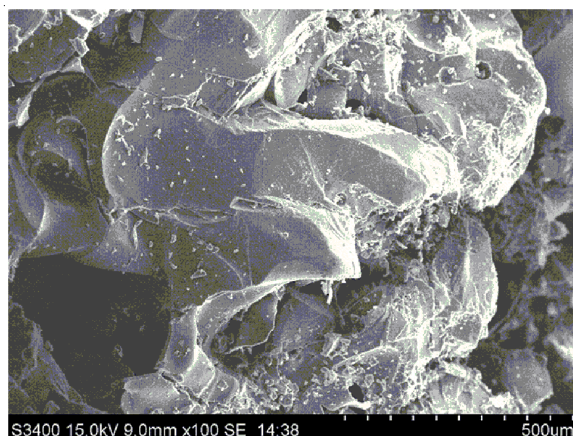
Items	Tensile strength (MPa)	Elongation at break (%)
Pure PVC	35.48	20.69
ESO/PVC	22.20	55.45
THEIC-SBOE/PVC	21.75	55.19

Flame retardancy tests: The chlorine content in PVC is high, endowing the polymer with excellent inherent flame resistance. However, the addition of a flammable plasticizer, such as dioctyl phthalate, will generate a flammable product. At a dioctyl phthalate content of 15 %, the limiting oxygen index of the PVC blend was only 23.5. The data in Table-4 show that with increasing amount of THEIC-SBOE, the limiting oxygen index increased. When the mass fraction of THEIC-SBOE reached 35 %, the limiting oxygen index of the PVC blend reached 28.4 %, indicating that the addition of THEIC-SBOE to PVC can greatly improve the flame retardancy. Hence, THEIC-SBOE shows good prospects for application as a flame-retardant plasticizer.

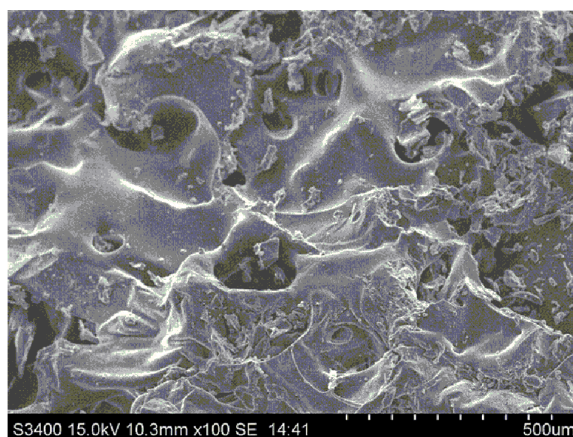
TABLE-4
RESULTS OF FLAME-RETARDANT PERFORMANCE TESTS

Items	1	2	3	4
PVC (phr)	100	100	100	100
DOP (phr)	15	0	0	0
THEIC-SBOE (phr)	0	15	25	35
Limiting oxygen index (%)	23.5	27.4	27.6	28.4

Analysis of the morphology of carbon residue: Scanning electron microscopy (SEM) images, acquired with an S-3400N microscope (Hitachi Co., Japan) of PVC/DOP (A) and THEIC-SBOE/PVC (B) char combustion layers are shown in Fig. 5. The carbon residue surface of PVC/DOP was relatively smooth after burning, whereas that of THEIC-SBOE/PVC appeared more pitted, which could be attributed to the release of volatile decomposition products on the surface in the latter case. Expansion



(a) Residue carbon of PVC/DOP



(b) Residue carbon of THEIC-SBOE/PVC

Fig. 5. Microstructure of residual carbon layers from PVC blends (100 × magnification)

of the carbon layer may prevent heat transfer and exclude oxygen, thereby effectively preventing flame spread. On this basis, THEIC-SBOE can be classed as an intumescent flame retardant.

Conclusion

A bio-based flame-retardant plasticizer, THEIC-SBOE, has been prepared from *tris*(2-Hydroxyethyl)isocyanurate (THEIC) and soybean oil methyl ester and its structure has been confirmed by ¹H NMR, ¹³C NMR and FTIR spectra, as well as by thermogravimetric analysis and elemental analysis. THEIC-SBOE has been found to exhibit satisfactory plasticizing and flame-retardant properties; at 15 % in PVC, the tensile strength was 21.75 MPa and the elongation at break was 55.19 %. The limiting oxygen index (LOI) of the PVC blend reached 28.4 % with the addition of 35 % (w/w) THEIC-SBOE. SEM analysis of the carbon residue from the PVC blend indicated that THEIC-SBOE could be classed as an intumescent flame retardant. This bio-based flame-retardant plasticizer would seem to have good prospects for application.

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