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Phosphorus Containing Rubber Seed oil as a Flame Retardant Plasticizer for Polyvinyl Chloride

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ABSTRACT

The application of phthalate plasticizers has been restricted around the world due to their poor migration and potential harm to the human body. Hence, producing functional bio-based plasticizers via exploiting clean and reusable resources meets the satisfaction of current demands. In this study, flame-retardant rubber seed oil-based plasticize (FRP) was prepared via epoxidation reaction and ring opening addition reactions, which was used as a flame-resistant plasticizer for polyvinyl chloride to replace petroleum-based phthalate plasticizer. When DOP was replaced with FRP, the torque of PVC blends increased from 11.4 to 18.4 N·m, the LOI value increased from 24.3% for PVC-FRP-0% to 33.1% for PVC-FRP-20. The THR value diminished from 39 MJ/m^2 (pertaining to PVC-FRC-0) to 22 MJ/m^2 Tg increased from 23°C to 47°C, the weight loss of plasticized PVC blends significantly reduced from 22.6% to 2.8% in leaching tests. The study provided a new way to prepare flame retardant plasticizer using rubber seed oil as raw material.

Nomenclature

DOP	Dioctyl Phthalate
FRC	Flame-retardant rubber seed oil-based plasticizer
PVC	Polyvinyl chloride
RSO	Rubber seed oil
LOI	Limiting oxygen index
ERSO	Epoxy rubber seed oil
HRR	Heat release rate
THR	Total heat release (THR)
T_d	Temperature at 5% weight loss
T_{10}	Temperature at 10% weight loss
T_{50}	Temperature at 50% weight loss
T_g	Glass transition temperature

1 Introduction

Plasticizer has been widely used in the processing of polymers such as polyvinyl chloride (PVC) plastics. The most studied, most abundant, and perhaps most well-known plasticizers that are also emerging contaminants are phthalate plasticizer. The phthalate plasticizer derived from petroleum is the most widely used plasticizer in industrial production, but its application is increasingly limited in view of its potential menace to the surrounding environment even human health [1–3]. With the increasingly stringent global environmental protection regulations, environmental protection and safety have become a significant trend in the development of the plasticizer industry. Bio-based plasticizers specially used in the fields of medicine or health equipment, packaging, as well as environmentally friendly plasticizers with enhanced mechanical properties have been continuously developed [4–8]. Many bio-based plasticizers have been reported including isosorbide [9], cardanol [10–12], castor oil [13–15], lactic acid [16,17], and many kinds of vegetable oils [18–20].

Rubber seed oil (RSO) is extracted from rubber seed. The main component of RSO is triglyceride [5,21]. Bio-based plasticizer from RSO can be synthesized via esterification, epoxidation, and halogenation hydrolyzation reactions. Not only can the polar groups inside, including ester groups and ether groups, enhance the compatibility of plasticized PVC materials, but they also optimize physical property of PVC products in some respects [22,23]. Thus, reactions on RSO are carried out in order for the bio-based plasticizers synthesis, which can be taken as a promising and strategic research.

In this study, the rubber seed oil with rich reserves, wide sources and low price was selected as the raw material. The rubber seed oil was modified by epoxidation and ring opening addition reaction to synthesize the bio-based plasticizer products, which were used to replace the petroleum-based phthalate plasticizer; The mechanical properties, thermal properties, processability, flame-retardancy and extraction resistance of plasticized PVC blends were studied. The effect of partial substitution of the prepared oil-based plasticizer for phthalate plasticizers is studied to reduce the dependence of the plastic additives industry on petrochemical products.

2 Experimental

2.1 Materials

Dioctyl phthalate (DOP, 98%), diethyl phosphite (99%), N-hexane (97%), toluene (98%), triphenyphosphine (95%), dichloromethane (99%), ethyl acetate (99%), calcium stearate (Zn 10%–12%) and sodium chloride (99.5%) were bought from Aladdin reagent (Shanghai) Co., Ltd. (China). S-1100 PVC resin (no additives) was provided by Jinling Chemical Industry Co. (Nanjing, China). Rubber seed oil (RSO) was provised by Kuming Jinning Chemical Industry Co., Ltd. (China).

2.2 Synthesis of Epoxy Rubber Seed Oil (ERSO)

RSO was dissolved in dichloromethane and put in the a round bottom flask, which was put in the ice bath. 3-Chloroperoxybenzoic acid was dropped in the mixture (mole ratio of double bonds to 3-Chloroperoxybenzoic acid is 1:0.5). The reaction was kept stirring for 5 h at room temperature to obtain the raw product. The obtained raw product was dissolved in dichloromethane and washed with brine and distilled water, then dried by anhydrous magnesium sulfate ($MgSO_4$) and purified using silica gel column chromatography to obtain ERSO.

2.3 Synthesis of Flame-Retardant Rubber Seed Oil-Based Plasticizer (FRP)

ERSO (20 g) was dissolved in toluene (16 g), all of which were blended in a three-necked round-bottom flask. The mix of diethyl phosphate (6 g), triphenyphosphine (0.02 g) and toluene (16 g) were also put in the flask within 40 min at room temperature. Then, a 4 h-stir at 75°C was carried out. The reaction mixture was dropped to room temperature with sodium hydroxide (NaOH) solution and washed until pH = 7. FRP was

obtained via removing water by rotary-evaporation, after a 3-time-wash through distilled water. The synthesis of FRP was showed in Fig. 1.
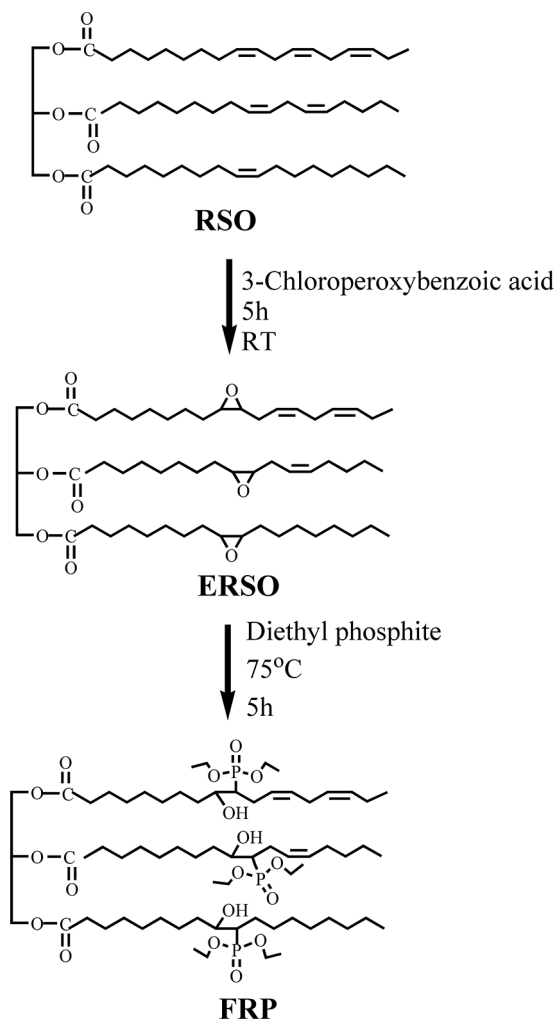

Figure 1: Synthesis of FRP

2.4 Preparation of FRP-Plasticized PVC Blends

FRP-Plasticized PVC blends were prepared by melt processing and the formulations were illustrated in Table 1. Then, further extrusion into strips like dumbbell or rectangular was necessary for subsequent tests.

Table 1: Detailed formulations of FRP-plasticized PVC blends

PVC blends	PVC (g)	DOP (g)	FRP (g)	Calcium stearate (g)
PVC-FRP-0	100	40	0	2
PVC-FRP-5	100	35	5	2
PVC-FRP-10	100	30	10	2
PVC-FRP-15	100	25	15	2
PVC-FRP-20	100	20	20	2

2.5 Characterization

RSO, ERSO and FRP were respectively illustrated through Fourier transform infrared spectrometer (FT-IR) (Nicolet 6700), with the chosen wavelength between 4000 and 500 cm^{-1}. ^{1}H nuclear magnetic resonance (^{1}H NMR) spectrums were presented with the solvent of $CDCl_3$ and internal standard of tetramethylsilane (TMS), respectively. Combustion tests were carried out according to GB/T 2406.1-2008. The FRP-modified PVC samples were designed into 80 mm × 10 mm × 4 mm. FTT200 cone calorimeter was used to analyze the combustion properties of samples that were cut into 100 mm × 100 mm× 2 mm, and ISO-5660 standard procedures would be referenced. The thermogravimetric analysis (TGA) was detected with surrounding N_2 in the flow rate of 50 mL/min. The heating rate of PVC blends was set to 10 °C/min from the beginning of 50°C to the final 600°C. The leaching tests related to plasticizers were examined in term of ASTMD1239-98 with N-hexane as the chosen solvent. The PVC blends were submerged into solvents at the temperature of 30°C for one week. Thereafter, the samples were removed and the surface solvent was wiped off. Then further drying was conducted at 50°C for whole day. The migration rate was calculated in term of the following Eq. (1):

$$Migration\ rate = (W_1 - W_2)/W_1 \tag{1}$$

Thereinto, W_1 and W_2 represent the front and rear weight, respectively.

In addition, the tensile rate of electronic tensile testing machine was set to 20 mm/min, and the dynamic mechanical analysis (DMA) was brought into effect to investigate the specific glass transition temperature (T_g), from −80°C to 100°C at a heating speed of 3 °C/min. Limiting oxygen index (LOI) values were measured on a JF-3 oxygen index measuring instrument.

3 Results and Discussions

3.1 Synthesis of FRP

FTIR spectra of RSO, ERSO and FRP were shown in Fig. 2. The characteristic peaks around 3007 cm^{-1} were associated with -CH=CH- in RSO [24,25]. As Compared with the spectra of ERSO, the characteristic peak of CH=CH- vanished, opposite to the -C-O-C vibration which could be observed at approximately 972 and 1062 cm^{-1}. All mentioned indicated that the -C=C- double bonds were converted into epoxy groups [26,27]. The peak at 1032 cm^{-1} was attributed to -P-O-CH- symmetric bending vibration, and -OH was observed at 3470 cm^{-1} in the FT-IR of FRP. The epoxy group at 972 and 1062 cm^{-1} cannot be observed in the FT-IR of FRP [28,29], which means that the reaction between P-OH and ERSO was accomplished.
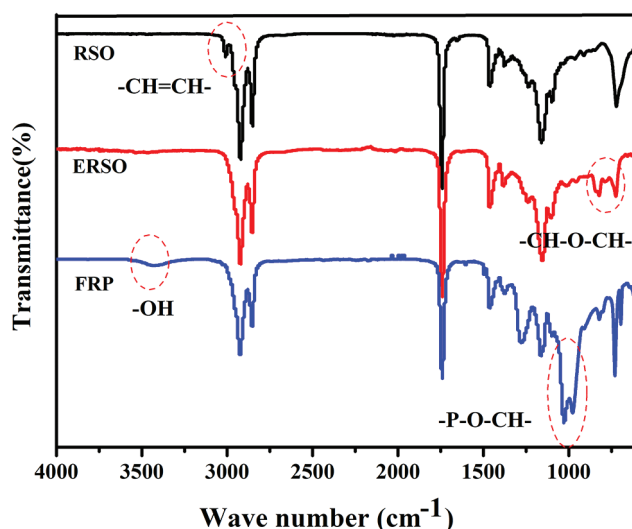

Figure 2: FT-IR of RSO, ERSO and FRP

The ^{1}H NMR spectrums pertaining to RSO, ERSO and FRP are exhibited in Fig. 3. The strong peak at δ = 5.28 ppm is attributed to the protons of -CH=CH- in RSO [25,26]. When epoxidation was finished, the peak at δ = 5.28 ppm became weak in the ^{1}H NMR spectrum of ERSO, because the epoxidation reaction was not complete, and an emerged peak at 2.95–3.20 ppm was assigned to protons on the epoxy groups of ERSO [26,27], which indicated that some -CH=CH- bonds of RSO were converted into epoxy groups. In the ^{1}H NMR spectrum of FRP, a new proton signal of -P-O-CH$_2$- appeared at δ = 2.3 ppm [28,29], and the protons signals in the 5.28 ppm associated with -C-O-C- bonds showed weaker than ERSO, which indicated that chemical structure of FRP contains phosphate groups, which indicated that FRP was synthesized successfully.
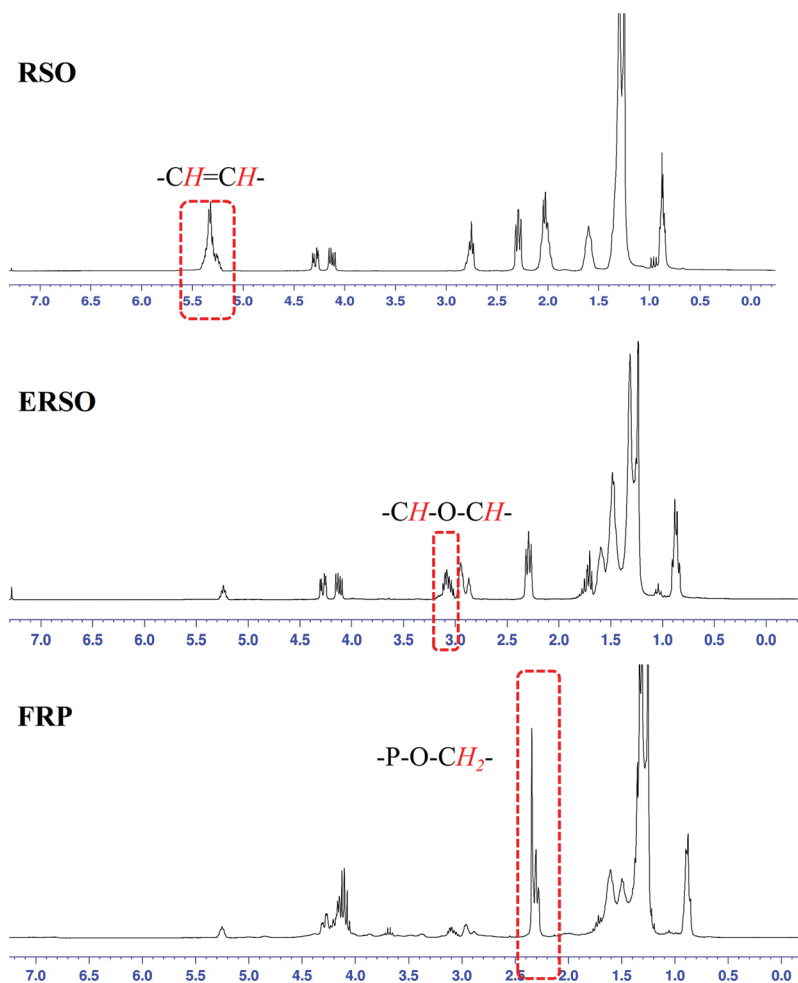

Figure 3: ^{1}H NMR of RSO, ERSO and FRP

3.2 Performance of Plasticized PVC Blends

The melting behavior was confirmed in the Haake chamber by gathering the processing data during the mix. Fig. 4 presents the torque values relevant to the proportion of plasticizer for the 5 min processing time. When more DOP was replaced with FRP, the torque of PVC blends increased from 11.4 to 18.4 N·m, respectively, corresponding to PVC-FRP-0 and PVC-FRP-20. In other words, 61% augmentation could be achieved, showing disadvantages in conduction of thermoplastic processing pertains to PVC blends.
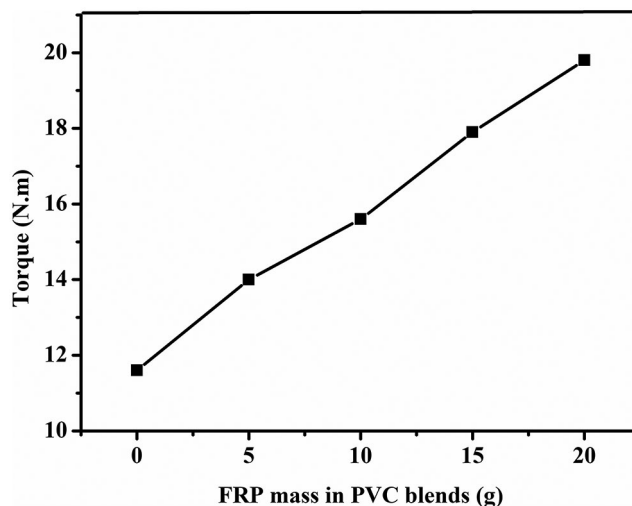
Figure 4: The torque data of plasticized PVC blends

FRP contains many flame-resistant phosphate groups, which could be used as a alternative to DOP as the flame-resistant plasticizer. The flame-resistance of plasticized PVC blends was conducted by the LOI tests and the variation with regard to FRP content was described in Fig. 5. When DOP was replaced with FRP in plasticized PVC blends, the LOI value increased from 24.3% for PVC-FRP-0% to 33.1% for PVC-FRP-20. Only the latter one exhibited greater value than 26.0%, to a certain extent, displaying self-blackout capacity. Generally, FRP is not suitable to be considered as a preferable flame retardant plasticizer in the PVC blends [30,31].
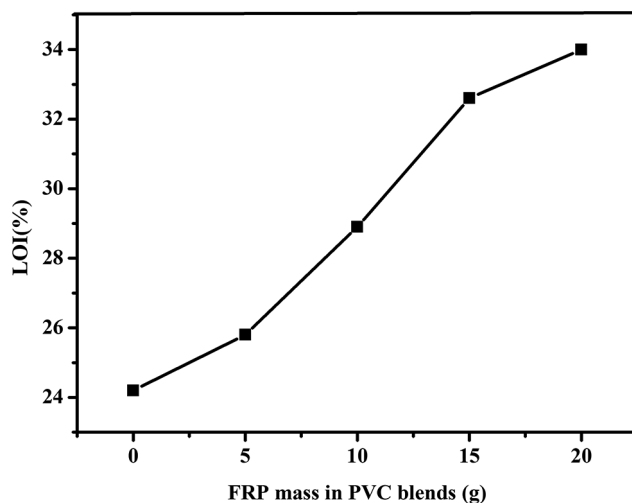

Figure 5: LOI data for plasticized PVC blends

PVC chemical structure contains a large amount of chlorine, which makes it hard to burn. However, it will combust and release much heat when PVC products plasticized with DOP, being blended into PVC. Fig. 6 showed the heat release rate (HRR) curves of plasticized PVC blends. There exists a notable difference in HRR curves between PVC-FRC-0 and PVC-FRC-20. Almost all HRR curve of PVC-FRC-0 is higher than PVC-FRC-20, which indicats that PVC-FRC-0 released heat faster than PVC-FRC-20.

Once ignited, PVC-FRC-0 produced flammable volatiles and released a lot of heat. However, the PPVC-FRC-20 was harder to burn than PVC-FRC-20. Thermal degradation of phosphate ester groups containing FRP produces a large amount of phosphoric acid and polyphosphate [31–33], which can promote carbon formation by removing water from FRP. The char residue will block heat transfer and the pyrolysis process. In addition, the total heat release (THR) curves of plasticized PVC blends were shown in Fig. 7. It can be found that the whole THR curve of PVC-FRC-0 was higher than PVC-FRC-20, which indicated that PVC-FRC-0 released more heat than PVC-FRC-20. The THR value decreased from 39 MJ/m^2 (pertaining to PVC-FRC-0) to 22 MJ/m^2 (pertaining to PVC-FRC-20) when 20 phr DOP was replaced with FRP in the plasticized PVC blends. All mentioned above revealed that FRP had capacity of improving the flame retardancy.
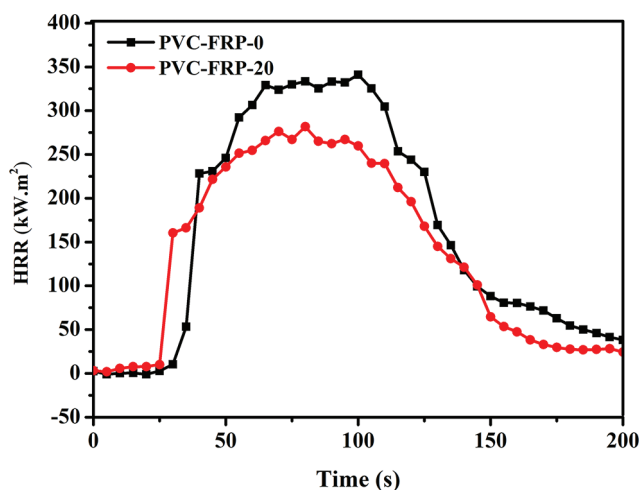

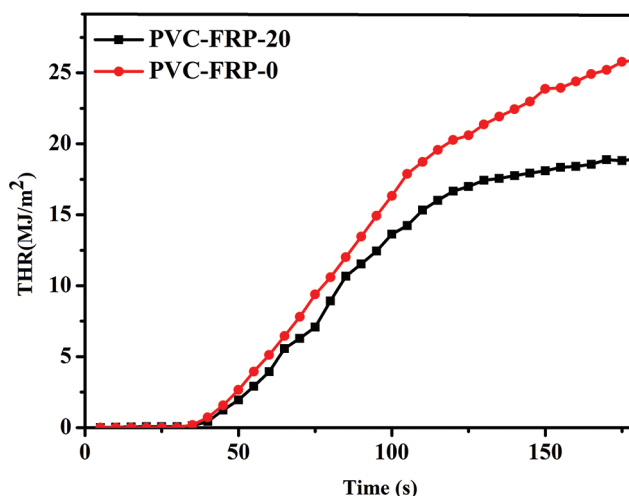Figure 6: HRR curves of plasticized PVC blends

Figure 7: Total heat released of FRP-plasticized PVC blends

The thermogravimetric loss data of plasticized PVC blends with different mass of plasticizers were shown in the Figs. 8 and 9, and Table 2. As is demonstrated in the Fig. 8, the degradation temperature (T$_d$: Temperature at 5% weight loss) of PVC blends increased with more DOP replaced by FRP, from the

initial content of 5% FRP. When PVC blends plasticized with 40 phr DOP, T_d is 252°C, while the T_d reached 272°C when PVC blends plasticized with 20 phr DOP and 20 phr FRP. In addition, the temperature at 10% weight loss (T_{10}) and the 50% one (T_{50}) showed the same increasing trend when DOP was replaced with FRP. This indicated that FRP can improve thermal stability of PVC blends. All plasticized PVC blends presented 3 stages in N_2 with regard to thermal degradation curves. None of the samples illustrated conspicuous weight loss until approaching 150°C. At stage one (from 150°C to 320°C), the weight loss process could be ascribed to the FRP migration together with the PVC dechlorination [34,35]. The temperature range belonging to the second stage was 320°C–450°C, which is mainly understood as the conversion process of conjugated olefins to aromatics. Finally curves between 450°C and 600°C corresponding to the fact that polyenes were cracked into olefin, as the third stage came out [34,35]. FRP had a considerable effect on preventing the weight loss of plasticized PVC blends. There exist numerous polar groups in plasticizer molecules that form hydrogen bonds with α-H of the PVC chain, deferring the PVC dechlorination [36,37].
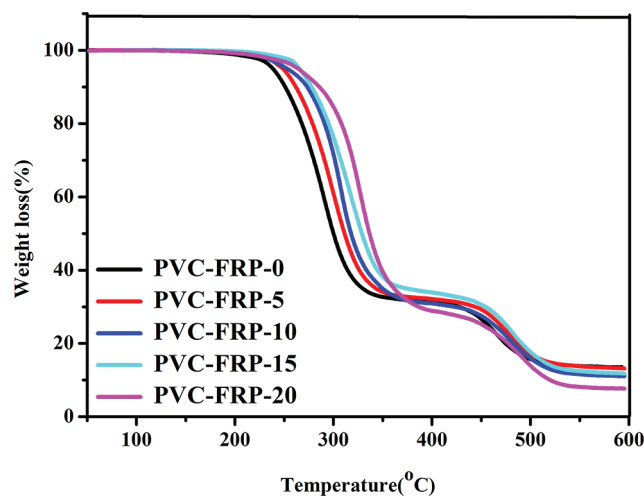

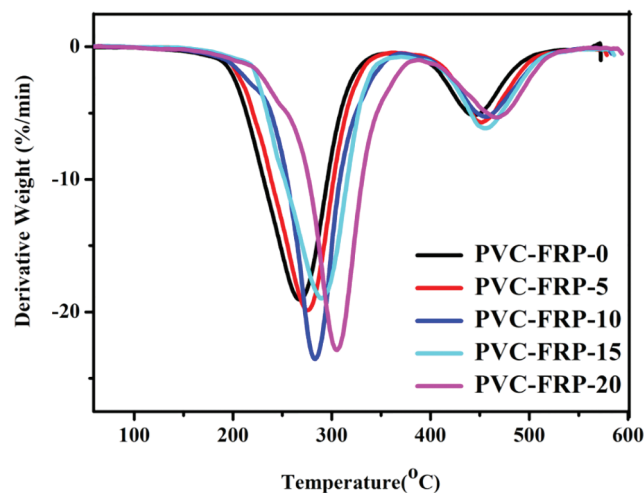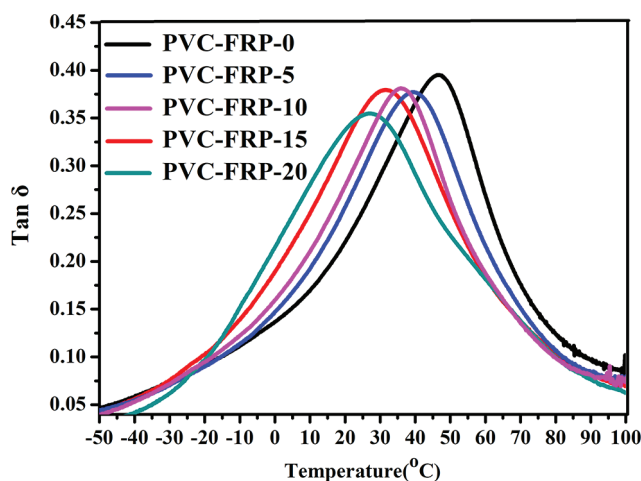**Figure 8:** TGA curves of FRP-plasticized PVC blends

Figure 9: DTG curves of FRP-plasticized PVC blends

Table 2: The TGA data of PVC blends

PVC blends	T_d (°C)	T_{10} (°C)	T_{50} (°C)	T_g (°C)
PVC-FRP-0	252	261	292	23
PVC-FRP-5	256	267	301	29
PVC-FRP-10	261	274	304	36
PVC-FRP-15	266	278	310	39
PVC-FRP-20	272	281	318	47

T_g partly mirrors the plasticizing property of the plasticizers. Fig. 10 shows the DMA curves of plasticized PVC blends containing different masses of FRP. Each curve has only a single peak, corresponding to a homogeneous system. It has been reported that the T_g value of the original PVC is approximately 85.8°C, indicating that adding DOP or FRP to PVC can prominently reduce the T_g value. When DOP was replaced with FRP gradually, T_g increased from 23°C to 47°C, which indicated that plasticized ability of FRP was lower than DOP.

Figure 10: DMA curves of FRP-plasticized PVC blends

Extraction resistance is an important quality in evaluating the migration property of plasticizers. The excellent extraction resistance can maintain the long-term stability of mechanical, thermal, electrical properties and flame-retardancy of plasticized polymer products, and prevent the potential threat to human health caused by the migration of plasticizers in the use of food and medical devices. Fig. 11 manifests the weight loss of plasticized PVC with DOP and FRP in N-hexane, the advantage of using N-hexane as solvent is that organic solvent can accelerate the migration of plasticizer, and then its migration performance can be evaluated in a short time [5]. With the gradual decrease of DOP and increase of FRP in PVC blends, the weight loss of plasticized PVC blends significantly reduced from 22.6% to 2.8%. FRP showed superior solvent extraction resistance than that of DOP. FRP with a larger relative molecular weight and higher branching degree has better migration resistance than DOP.

The tensile test was conducted at the temperature of 25°C to appraise FRP's plasticizing effect, with the detailed results being exhibited in Table 3. The affixion of plasticizer usually increases elongation at break and decreases the tensile strength of plasticized PVC materials. Furthermore, when DOP was replaced gradually with FRP, the elongation at break of plasticized PVC blends decreased from 450% to 19%,

seeing an opposite trend to the tensile strength, from 12.3 to 28.9 MPa. The results indicated though the ester groups and phosphate groups in the structure of FRP have the lubrication effect on PVC chains, making plasticized PVC blends more flexible [38,39], but FRP showed a lower plasticizing effect than DOP.
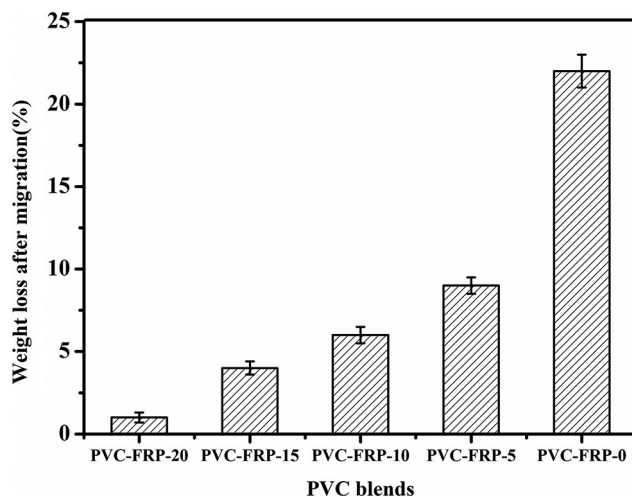

Figure 11: Migration property of FRP

Table 3: The detailed mechanical parameter of PVC blends with different contents of FRP

PVC blends	Tensile strength (MPa)	Elongation at break (%)
PVC-FRP-0	12.3 ± 2.0	450 ± 25
PVC-FRP-5	16.8 ± 1.5	238 ± 13
PVC-FRP-10	21.0 ± 2.1	189 ± 9
PVC-FRP-15	23.1 ± 1.5	89 ± 6
PVC-FRP-20	28.9 ± 2.3	19 ± 3

4 Conclusions

In this study, phosphorus-containing rubber seed oil was prepared via epoxidation reaction and ring opening addition reactions, which was used as a flame-retardant polyvinyl chloride plasticizer to replace petroleum-based phthalate one. In plasticized PVC blends, the torque of PVC blends increased from 11.4 to 18.4 N·m after DOP was replaced by FRP at the content of 20 phr, which indicate the addition of FRP is unfavorable to the thermoplastic processing process. But the LOI value, at the same time, increased from 24.3% to 33.1%, and the THR data decreased from 39 to 22 MJ/m^2, which indicated that FRP in the plasticized PVC blends reduced the flammability. As a result of hydrogen bond formation, with the coaction of α-H in PVC molecular chains and polar groups in plasticizers, the dichlorination of PVC will be intervened to delay. With the addition of DOP or FRP, PVC can significantly raise the T_g value from 23°C to 47°C. It means the plasticized ability of FRP was lower than DOP, though FRP still has the potential to be a flame retardant and secondary plasticizer for PVC materials. FRP with the larger relative molecular weight and higher branching degree has better migration resistance than DOP. When DOP was replaced gradually with FRP. In all, the bio-based plasticizer from RSO can be used as a flame-retardant plasticizer to partly replace DOP in PVC blends.

Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

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