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Synthesis and properties of chlorine and phosphorus containing rubber seed oil as a second plasticizer for flame retardant polyvinyl chloride materials

Huabei Li[1,2], Xiaolin Wang[3], Xinding Yao[1,2], Hongying Chu[1,2*]

[1]*Yellow River Conservancy Technical Institute, Kaifeng 475004,China*
[2]*Henan Engineering Technology Research Center of Green Coating Materials, Kaifeng 475004,China*
[3]*Henan Technical Institute, Kaifeng 475000,China*
[*]*Corresponding author: e-mail: hongyingchu@163.com*

The synthesis of multifunctional plasticizer using rubber seed oil can increase its added value and expand the application field of plasticized products. Recent studies on bio-based plasticizers focus on bio-based raw materials but products lack functionality. In this study, flame retardant phosphate and chlorine were introduced into the chemical structure of rubber seed oil to synthesis a nitrogen and phosphorus synergistic flame retardant plasticizer based on rubber seed oil(NPFP) and apply it to plasticize polyvinyl chloride (PVC). Thermal stability, limiting oxygen index, plasticizing property, solvent extraction resistance, and microstructure of plasticized PVC materials were characterized. The results showed that NPFP with excellent solvent extraction resistance can significantly enhance the limiting oxygen index and thermal stability of plasticized PVC materials, and can partially replace dioctyl phthalate(DOP) as multifunctional auxiliary plasticizer.

Keywords: Flame retardant Plasticizer; Rubber seed oil; Polyvinyl chloride; Flame retardant performance.

INTRODUCTION

In the early 19th century, plasticizers have been used to change the properties of polymers. Celluloid or celluloid paint manufacturers use natural camphor and castor oil as plasticizers[1]. In 1912, triphenyl phosphate was used to replace camphor oil as ester plasticizers. Phthalate esters were introduced as plasticizers in 1930[2]. Phthalate plasticizers have been used as the most widely used plasticizers in the past decades in building materials, toys, food packaging, blood bags, wires and cables and other aspects of clothing, food, housing, and transportation since 1930[3]. With the development of the plastic industry, the wide application of plastic products has led to the development of plasticizers to meet large-scale applications. In the early 1980s, people gradually realized the harm of phthalate plasticizers to human body and the environment and began to introduce restrictions and regulations, which caused the rapid development of bio-based plasticizers[4]. Non-toxic and environment-friendly plasticizers with biodegradability and excellent plasticizing properties from biomass resources is the future development direction. It has been widely reported that soybean oil[5], castor oil[6], cardanol[7–9], rosin[10], waste cooking oil[11–12], fatty acid[13], eugenol[14,] and tung oil[15–17] were used to synthesis bio-based plasticizers. Using biomass resources to synthesize plasticizers can replace petrochemical resources, and the introduction of biomass resources can also reduce pollution.

Rubber seed oil(RSO) is extracted from rubber seed, which can be used to synthesis epoxidized rubber seed oil(ERSO) plasticizer via epoxidation reaction[18–19]. Because of the existence of unsaturated double bond, it can introduce different functional groups at the unsaturated bond position, and then obtain fine chemicals and polymer materials, or make the unsaturated bond react with other polymers to achieve the purpose of polymer modification. RSO is relatively cheap compared with petrochemical raw materials, and it is a plasticizer in itself. Based on RSO and combined with other chemical reagents, various plasticizers with different functions can be synthesized[20]. ERSO has epoxy groups in its molecular structure and shows strong reactivity. It is easy to undergo ring-opening reaction or molecular chain growth after an addition reaction with other chemical compounds.

In this study, we used RSO as raw material to synthesis flame retardant plasticizer. The flame retardant phosphate and chlorine were introduced into its chemical structure, which was used to plasticize polyvinyl chloride(PVC). The performances of plasticized PVC materials were characterized. It was expected that the obtained nitrogen and phosphorus synergistic flame retardant plasticizer based on rubber seed oil(NPFP) can enhance the performance of plasticized PVC materials.

EXPERIMENTAL SECTION

Materials

Dioctyl Phthalate (DOP, 98%), aluminum trichloride, phosphorus oxychloride, N-hexane, calcium stearate and sodium chloride were bought from Aladdin reagent (Shanghai) Co., Ltd. PVC (S-1100) was provided by Jinling Chemical Industry Co. (Nanjing China). Rubber seed oil(RSO) was provided by Kuming Jinning Chemical Industry Co., Ltd.

Synthesis of epoxy rubber seed oil(ERSO)

ERSO was synthesized according to our recent study[20], as seen in Figure 1.

Synthesis of nitrogen and phosphorus synergistic flame retardant plasticizer based on rubber seed oil(NPFP)

Aluminum trichloride and phosphorus oxychloride was added into a reaction flask, the mixture was slowly stirred and heated to 50 °C, then ERSO was dropped in the reaction flask for 2 hours. The mole ratio of ERSO to phosphorus oxychloride was 3:2. The temperature was then heated to 60 °C and stirred for another 3 h. NPFP was obtained after washing to neutral with distilled water

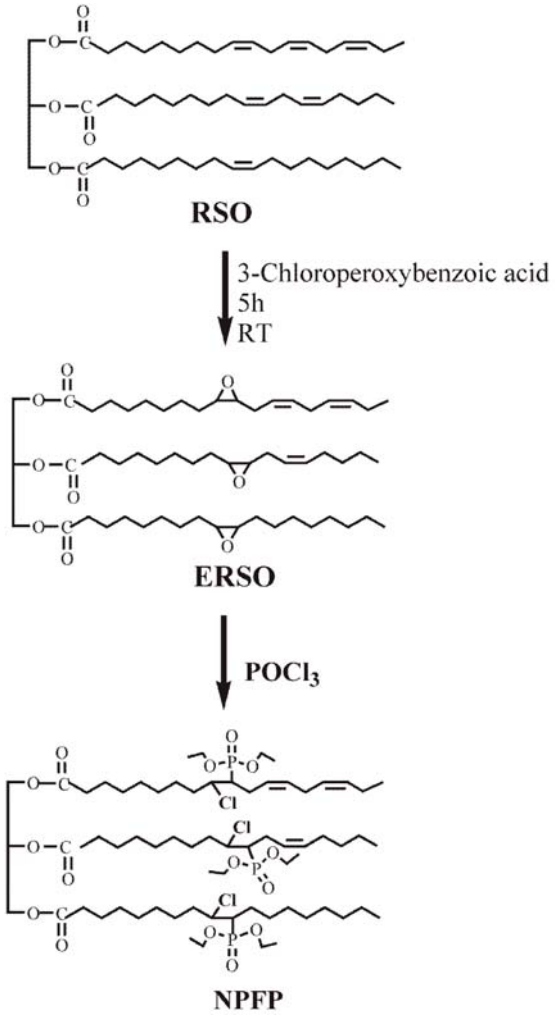


Figure 1. Synthesis of NPFP

and removing water via vacuum distillation at 60 °C. Figure 1 shows the synthetic route.

Preparation of plasticized PVC materials

PVC was blended with plasticizers according to the formula in Table 1. A certain mass of mixture is thermoplastic blended in the torque rheometer at 165 °C for 5 min. Then a micro-injection molding machine was used to process the thermoplastic mixture at 165 °C under 550 MPa. Dumbbell and strip samples were prepared for testing.

Table 1. Formulation of plasticized PVC materials

Plasticized PVC materials	PP-30%	PP-40%	PP-50%	PP-60%
PVC(g)	100	100	100	100
DOP(g)	30	20	10	0
NPFP(g)	30	40	50	60
Calcium stearate/zinc stearate(g)	1/1	1/1	1/1	1/1

Characterization

Fourier Transform Infrared spectroscopy (FT-IR) was investigated on a Nicolet 6700 Fourier transform infrared spectrometer. Hydrogen nuclear magnetic resonance (^{1}H NMR) was recorded on a BRUKER AVANCE III HD 400 MHz. Combustion tests were carried out by an Oxygen index (JF-3, Nanjing Lei instrument Co. Ltd., China). Thermogravimetric analysis (TGA) was detected by a 1100SF TG instrument (Mettler-Toledo Co., Switzerland) in N_2 atmosphere a flow rate of 50 mL/min. Temperature was heated from 50 °C to 600 °C at a heating rate of 10 °C/min. Solvent extraction tests were carried out according to our recent study[19].Volatility of ERSO were carried out according to our recent study[19–20], which was evaluated by placing plasticized PVC samples in a convection oven at 70 °C for 24 h and cooled to room temperature in a desiccator for 2 h. The weight changes were measured before and after the heating. Mechanical properties were determined according to ISO 527-5:2009 on an electronic tensile testing machine (Xinsansi Co., China). There are five dumbbell samples for every plasticized PVC materials for testing tensile strength. The dynamic mechanical analysis (DMA) was carried out using a Q800 dynamic thermomechanical analyzer (TA Company, America) under a N_2 atmosphere(Heating rate: 3 °C/min, temperature range: –80 °C to 100 °C).

RESULTS AND DISCUSSION

Synthesis of NPFP

The chemical structure of RSO, ERSO and NPFP was investigated with FTIR and ^{1}H NMR. FTIR and ^{1}H NMR of RSO and ERSO has been reported in our previous study[20]. FTIR and ^{1}H NMR of NPFP are shown in Figure 2 and Figure 3. As seen in Figure 2, the absorption peak of -C=O is found at 1742 cm^{-1}, the absorption peaks at 2853 and 2921 cm^{-1} are attributed to -CH- and -CH_2- in the fatty acid chain of NPFP[19–20]. The most obvious absorption peak in the infrared spectrum of NPFP appears at 1099 cm^{-1}, where is the vibration absorption peak of P-O-C, the vibration absorption peak of P-O appears at 823 cm^{-1} [21]. In the ^{1}H NMR of NPFP, the peak at 0.82 ppm is attributed to protons of -CH_3- from NPFP, the peak remains unchanged throughout the epoxidation and ring opening reaction. The strong peak at 1.20 ppm corresponds to protons of -CH_2- on the glyceride backbone chain of NPFP. The peaks at 2.27, 2.92 and 3.02 ppm corresponded to other protons of -CH_2-[19–21]. Compared with our previous study, NPFP was obtained.

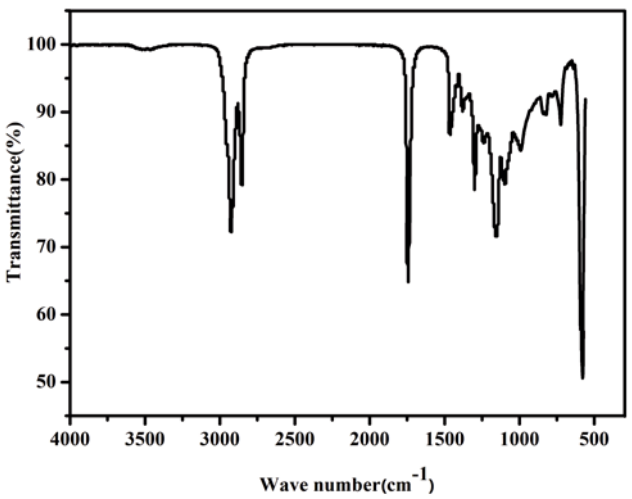


Figure 2. FT-IR of NPFP

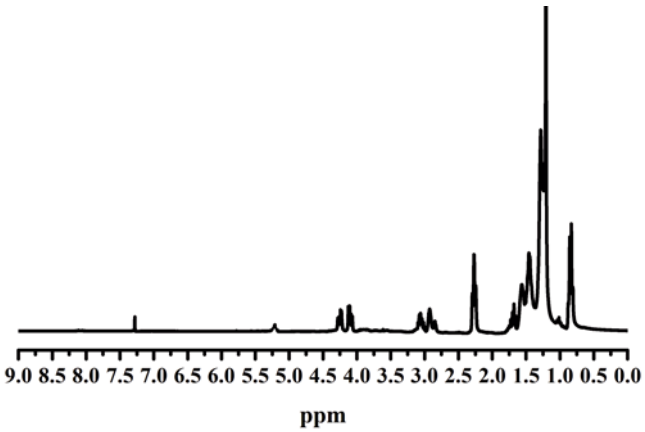


Figure 3. ^{1}H NMR of NPFP

Performance of plasticized PVC materials

Torque values of plasticized PVC materials were collected during the process of thermoplastic blending and showed in Figure 4. Torque is important to evaluate processability, compatibility and plasticizing performance. The lower torque means that plasticized PVC materials are easy to process, compatibility of PVC and plasticizer is more superior and plasticizing performance is better[22]. In this study, when the mass of NPFP increased from 30 g to 60 g, the torque value increased from 13.2 N · m to 22.8 N · m, which is 72.7% increment. The increase in torque is unfavorable to the thermoplastic processing of PVC materials, and will increase energy consumption.

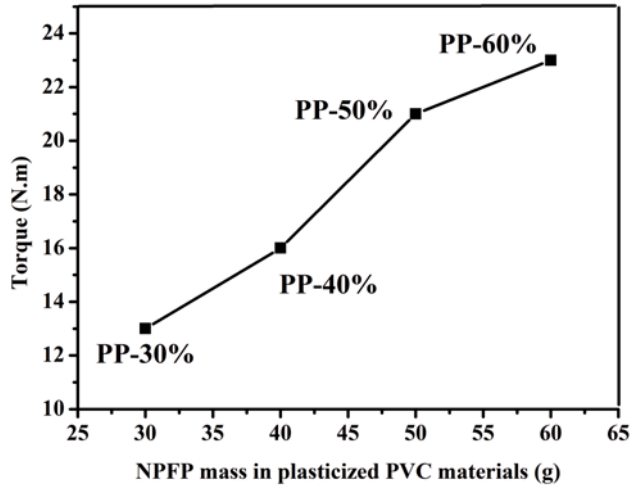


Figure 4. The torque data of plasticized PVC materials

Most phosphorus-containing flame retardant plasticizers have the advantages of low smoke and non-toxicity[23]. The flame retardant mechanism is that phosphoric acid is formed as a dehydrating agent and promotes the formation of carbon[24]. The formation of carbon reduces heat transfer. Phosphoric acid can absorb heat because it prevents the oxidation of CO to CO_2 and inhibits the heating process. The thermal decomposition of phosphorus-containing flame-retardant plasticizers produces metaphosphate, phosphoric acid and polymetaphosphate. Polymetaphosphate is a stable compound that is not volatile and has strong dehydration property, and is isolated from the air on the polymer surface. Chlorine-containing flame-retardant plasticizer mainly plays a flame-retardant role in the gas phase[25]. Because the hydrogen chloride gas produced by the decomposition of chloride is not easy to burn, it has the function of isolating air and heat. Hydrogen chloride can inhibit the chain reaction of polymer material combustion and play a role in scavenging free radicals[26]. In addition, chlorine-containing flame retardant plasticizer has excellent compatibility with PVC. In this study, the flame retardant performance of NPFP was detected with an oxygen index, the results are shown in Figure 5. When the mass of NPFP in plasticized PVC materials increased to 60 g, LOI increased from 26.2% to 36.1%. The phosphorus and chlorine-containing NPFP is a multifunctional nitrogen phosphorus synergetic flame retardant plasticizer.

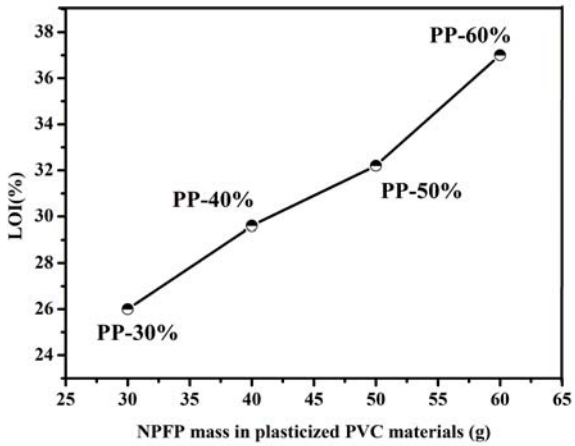


Figure 5. LOI data for plasticized PVC materials

Thermal stability of plasticized PVC materials was detected (Figure 6, Figure 7 and Table 2). When the mass of NPFP in plasticized PVC materials increased from 30 g to 60 g, the degradation temperature(T_d) increased from 231 °C to 252 °C, and the T_{50} increased from 297 °C to 319 °C, char residue also increased from 9.2% to 24.1%. These data suggested that NPFP can inhibit the degradation of PVC. All plasticized PVC materials showed similar TGA and DTG curves including two degradation stages, one is dechlorination and the other is the conversion of conjugated olefins to aromatics[27]. However, it can be found that NPFP delayed the degradation of PVC materials.

Tg is usually to evaluate the plasticizing property of plasticizers[28], the lower Tg for plasticized PVC materials means higher plasticizing property. Tg is an inherent property of plasticized PVC materials and a macroscopic

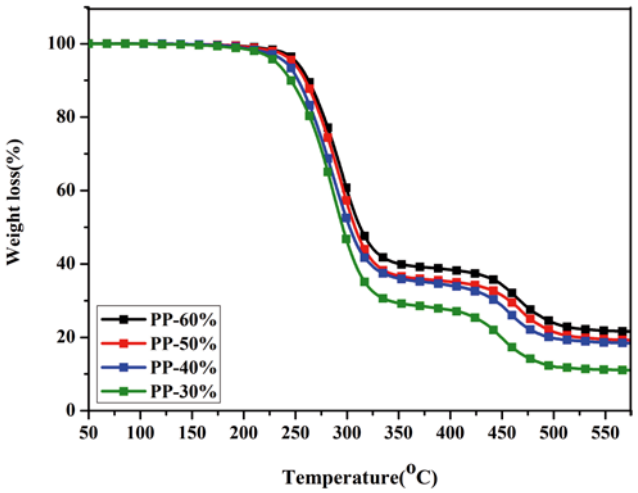


Figure 6. TGA curves of plasticized PVC materials

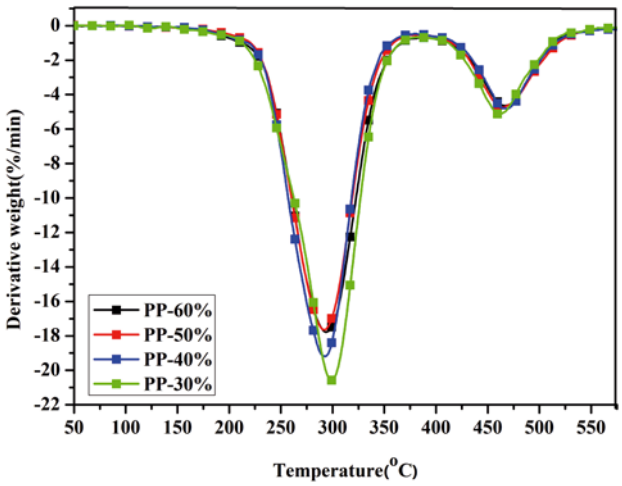


Figure 7. DTG curves of plasticized PVC materials

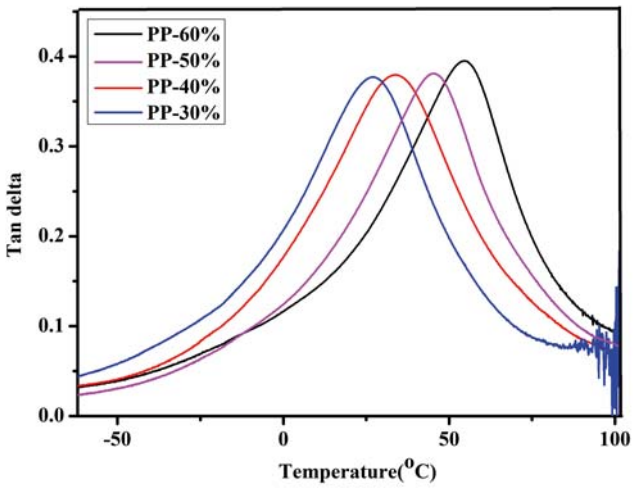


Figure 8. DMA curves of plasticized PVC materials

Table 2. The parameters of TGA and DMA of plasticized PVC materials

Plasticized PVC materials	T_d(°C)	T_{50}(°C)	Char residue(%)	Tg(°C)
PP-30%	231	297	9.2	25.4
PP-40%	237	303	14.5	32.5
PP-50%	248	312	16.3	46.1
PP-60%	252	319	24.1	53.6

reflection of the transformation of polymer movement form. It directly affects the use performance and technological performance of plasticized PVC materials.Tg is directly related to the flexibility of the molecular chain. The lower Tg, the greater the flexibility of the molecular chain. We investigated the Tg with DMA and the results are shown in Figure 8 and Table 2. When the mass of NPFP in plasticized PVC materials increased from 30 g to 60 g, Tg value increased from 25.4 °C to 53.6 °C, the results showed that plasticizing property of NPFP was lower than DOP. The reason is that the higher relative molecular weight and branching degree of NPFP than DOP inhibited the movement of PVC chain. However, only one Tg for all plasticized PVC materials indicated that DOP and DPFP have excellent compatibility with PVC. In addition, the superior flame retardant performance of NPFP makes it a second plasticizer.

Compatibility of PVC and plasticizer can be observed via metallographic microscope, which has been widely reported in recent studes[17, 20, 27]. In this study, we used a Leica metallographic microscope to investigate the microstructure of plasticized PVC materials in reflection mode and transmission mode(Figure 9 and Figure 10). It can be observed that when DOP was replaced with NPFP, the number of cracks and micropores on the surface of plasticized PVC materials increased, which

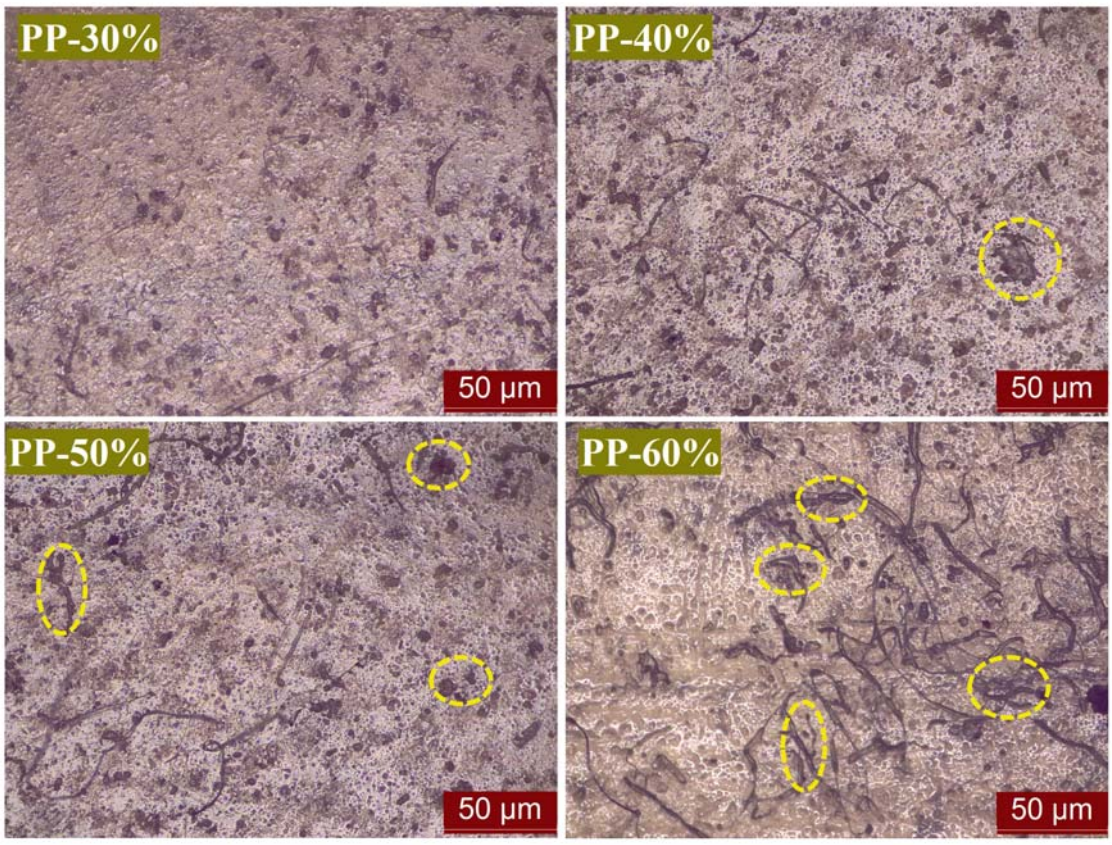


Figure 9. Microstructure of plasticized PVC materials detected by metallographic microscope in reflection mode

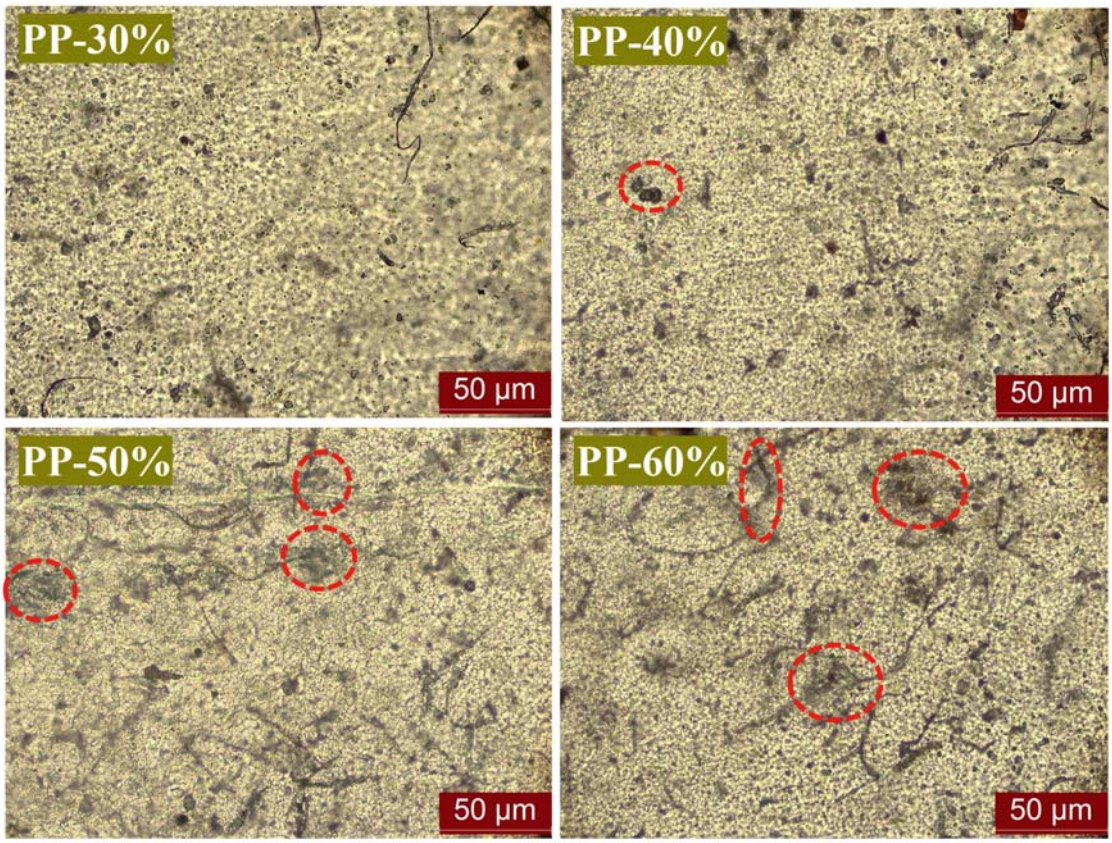


Figure 10. Microstructure of plasticized PVC materials detected by metallographic microscope in transmission mode

indicated that DOP is more compatible with PVC than NPFP. The results are consistent with DMA.

The extraction resistance of plasticizers refers to that plasticized PVC materials are immersed in liquid media (such as water, soap, oil, and chemical solvents), and plasticizers tend to migrate from plasticized PVC materials to the liquid media. This migration tendency depends on the properties of the plasticizer itself, such as the structure, polarity and molecular weight of plasticizers, and on the physical and chemical properties of the liquid medium in contact with plastics[29–31]. The basic properties of extraction resistance usually include oil resistance, solvent resistance, water resistance and soapy water resistance. Plasticizers are easily extracted by gasoline or oil solvents. Polar plasticizers with more phenyl and ester groups and plasticizers with more alkyl branched chains are difficult to be extracted by oil, because plasticizer molecules are more difficult to diffuse in the system. In this study, we used N-hexane as solvent to investigate the extraction resistance of NPFP, the results are shown in Figure 11, when DOP was gradually replaced with NPFP, the migration rate of plasticizers decreased from 5.42% to 2.18%. Volatility test was also carried and the results showed that when DOP was gradually replaced with NPFP, the weight loss for PP-30%, PP-40%, PP-50% and PP-60% was 4.81±0.34%, 3.47±0.19%, 3.48±0.30%and 2.93±0.12%. The decrease in migration rate indicated that NPFP has more excellent extraction resistance than DOP due to its larger relative molecular weight and higher branching degree than DOP.

Tensile strength and elongation at the break of plasticized PVC materials are shown in Table 3. The results showed when DOP was replaced with NPFP in plasticized

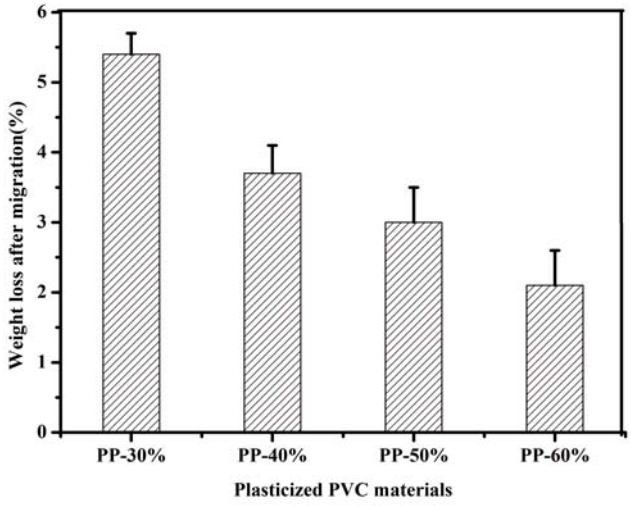


Figure 11. Extraction resistance of NPFP

PVC materials, the tensile strength of plasticized PVC materials increased from 10.2±1.2MPa to 19.13±1.4MPa, and elongation at break decreased from 254.3±11.2% to 198.4±12.5%. The polar groups such as ester groups of NPFP interact with the α-H of PVC to form a hydrogen bond, Thus, the acting force between PVC chains is weakened, and the purpose of plasticizing is achieved. Though the phosphate ester structure and chlorine of

Table 3. The mechanical properties of PVC materials

Plasticized PVC materials	Tensile strength (MPa)	Elongation at break(%)
PP-30%	10.2±1.2	254.3±11.2
PP-40%	14.12±1.1	232.0±6.7
PP-50%	16.56±1.0	212.4±8.2
PP-60%	19.13±1.4	198.4±12.5

NPFP can form a hydrogen bond with α-H of PVC to play plasticizing effect on PVC, the plasticizing effect of NPFP is lower than DOP.

CONCLUSION

In this study, we synthesized a synergistic flame retardant plasticizer from RSO, which was used to plasticize PVC. The results showed when the mass of NPFP in plasticized PVC materials increased from 30 g to 60 g, the torque value increased from 13.2 N · m to 22.8 N · m, LOI value increased from 26.2% to 36.1%, T_d increased from 231 °C to 252 °C , T_{50} increased from 297 °C to 319 °C, char residue increased from 9.2% to 24.1%, Tg value increased from 25.4 °C to 53.6 °C, tensile strength of plasticized PVC materials increased from 10.2±1.2 MPa to 19.13±1.4 MPa, and elongation at break decreased from 254.3±11.2% to 198.4±12.5%. The migration rate of plasticizers decreased from 5.42% to 2.18%. Though NPFP showed lower plasticizing efficiency than DOP, the excellent flame retardancy and solvent extraction resistance make it to be a multifunctional auxiliary plasticizer.

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