Synthesis of a Novel Bio-Oil-Based Hyperbranched Ester Plasticizer and Its Effects on Poly(vinyl chloride) Soft Films

Jie Chen,* Xiaoan Nie, and Jianchun Jiang

ABSTRACT: A novel hyperbranched ester plasticizer (SOHE) was synthesized from soybean oil. FTIR, 1H NMR, and 13C NMR spectroscopies were used to analyze the chemical structure of SOHE. SOHE was added into poly(vinyl chloride) (PVC). Thermal, mechanical, and dynamic mechanical properties of PVC samples were studied with thermal gravimetric analysis, dynamic mechanical analysis, and tensile tests. The results of SOHE substitution of petroleum-based diocyl phthalate (DOP) in soft PVC samples were studied. The results indicated that PVC blends mixed with the obtained plasticizer showed higher thermal stability and flexibility. When DOP was completely replaced with SOHE, the T<sub>j</sub>, T<sub>10</sub>, and T<sub>50</sub> of the films were raised to 267.5, 275.3, and 338.0 °C, respectively. The plasticizing mechanism was also investigated. The volatility resistance and extraction were studied, which results indicated that the migration stability of PVC samples was significantly enhanced with the increasing amount of SOHE.

1. INTRODUCTION
To obtain the desired flexible PVC products, more than 80% plasticizers are used in PVC processing as additives, which could be applied to medical devices, pipes, coatings, films, and so on. 1-4 The commercial plasticizer DOP is the usual main plasticizer, which is limited by the law due to its high risk of biological effects and toxicity on humans. 5 Furthermore, because of easy diffusion to surroundings from PVC resin, phthalates have an environmental impact, which also reduce the durable performance of PVC products. 3,6-8 In addition, research on environmentally friendly alternative plasticizers has been triggered by environmental concerns. 9-12 Soybean oil is a renewable low-cost and commonly used agricultural resource. From it, we can derive epoxidized soybean oil (ESO), polyesters, and modified polyurethane, which can be widely used in industries. It is reported that ESO is generally used as a reactive modifier, diluent, and plasticizer or stabilizer for PVC. 13-15 However, ESO presents poor migration stability for use in large doses, which is usually used in lower amounts as a secondary plasticizer.

Highly branched esters have improved plasticizer migration compared to DOP, which also have lower toxicity. 16 Kwak et al. developed bio-based alkyl terminal hyperbranched polyglycerols and highly branched polycaprolactone/glycidol copolymeric plasticizers. 16,17 The prepared PVC films showed excellent flexibility and solvent extraction resistance, showing potential in replacing DOP. 16 Hai et al. did work on synthesis of castor oil-based hyperbranched esters, 18 which have improved plasticizing effects, volatility resistance, and solvent extraction resistance. However, there are unreacted double bonds in the obtained hyperbranched ester plasticizer, which might reduce the compatibility of plasticizers and PVC. 16,17

We provided a novel soybean oil-based plasticizer, a hyperbranched ester plasticizer (SOHE), in this work (Figure 1). This plasticizer was blended into PVC as the main plasticizer or a secondary plasticizer for DOP. A wide range of PVC sample properties, such as thermal properties, dynamic mechanical properties, mechanical properties before and after aging, and migration properties, was investigated. According to our study, SOHE could prove to be a promising candidate for an alternative renewable plasticizer.

2. RESULTS AND DISCUSSION

2.1. Characterization. In Figure 2, the chemical structure of SOHE was analyzed with FTIR and compared with SOL and SOH. In the spectrum of SOL, the peak at 3442 cm<sup>-1</sup> corresponded to an absorption peak of O−H. The strong absorption at 1737 cm<sup>-1</sup> was attributed to a carbonyl group. Furthermore, the absorption peak at 3456 cm<sup>-1</sup> in the curve of SOH appears to be stronger than that of SOL, which indicated...
that more O–H groups appeared in SOH. For SOHE, the characteristic absorption peak around 3456 cm\(^{-1}\) had disappeared. The peaks of carbonyl groups at 1742 cm\(^{-1}\) appeared to be stronger than those of SOH and SOL. These illustrated that the ester groups were obtained. The results implied that the soybean oil-based polyol SOH had been converted into ester by esterification, and the hyperbranched ester was prepared.

Figure 3 shows the \(^1\)H NMR spectra of SOL, SOH, and SOHE. As seen from Figure 3a, the peak at 0.89 ppm (peak 1) was assigned to protons of methyl groups. The peak at 1.32 ppm (peak 2) and peaks at around 1.40–3.00 ppm (peaks 8, 5, and 9) corresponded to protons of methylene. The peaks at 3.00–4.50 ppm (peaks 10, 6, 7, 3, 4, and 12) corresponded to the protons of methylene groups of glyceride with the methyne connected to hydroxyl groups and methoxy groups. In Figure 3b, the peaks at 2.08–4.21 ppm (peaks 3, 3’, and 3”) corresponding to the protons of the methylene and methyne linked with hydroxyl were stronger than those of SOL, which indicated that the polyol was produced. Figure 3c shows the
1H NMR of SOHE. The chemical shift at 2.04 ppm (peak 1') was attributed to protons of methyl groups linked with carbonyl groups. The new peak at 5.26 ppm (peak 11') corresponded to the protons of methyne groups connected to carbonyl. These results suggested that the hyperbranched ester was prepared.

2.2. Thermal Stability. Figure 4 displays the TGA spectrum of SOHE and DOP heated in nitrogen at the rate of 10 °C/min. In Table 2, the initial decomposition temperature ($T_d$), 10% and 50% mass loss temperatures ($T_{10}$ and $T_{50}$), and weight loss are summarized. It can be seen that SOHE had increases of 137.3, 104.8, and 129.6 °C compared with DOP in $T_d$, $T_{10}$, and $T_{50}$ respectively. It can be summarized that the plasticizer SOHE shows better thermal stability.

Figure 5 shows the results of PVC samples with different contents of SOHE. The degradation data of $T_d$, $T_{10}$, and $T_{50}$ and weight loss data at different times are summarized in Table 1. There are two main degradation steps in the degradation curve of PVC samples. It can be seen in the first stage that the largest weight loss of 69.7% is at 200−350 °C.

![Figure 2. FTIR spectra of SOL, SOH, and SOHE.](figure2.png)

![Figure 3. 1H NMR spectra of (a) SOL, (b) SOH, and (c) SOHE.](figure3.png)

![Figure 4. TGA curves of SOHE and DOP.](figure4.png)

![Figure 5. TGA curves of the PVC samples with different plasticizers.](figure5.png)

| Sample | $T_d$ (°C) | $T_{10}$ (°C) | $T_{50}$ (°C) | 200−350 (°C) | 400−500 (°C) |
|--------|------------|--------------|--------------|-------------|-------------|
| DOP    | 224.3      | 223.1        | 263.3        | 69.7        | 16.1        |
| SOHE   | 361.6      | 327.9        | 392.9        | 66.6        | 17.4        |
| F1     | 41.46      | 226.0        | 239.2        | 69.7        | 16.1        |
| F2     | 45.68      | 260.7        | 256.9        | 66.6        | 17.4        |
| F3     | 46.82      | 259.2        | 304.4        | 64.9        | 19.4        |
| F4     | 51.57      | 263.3        | 314.3        | 62.5        | 20.8        |
| F5     | 61.89      | 275.4        | 321.8        | 59.8        | 21.6        |

Table 1. Thermal Properties of PVC Samples with Different Plasticizers

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Furthermore, the second step has the largest weight loss of 21.6% at 400−500 °C. The $T_p$, $T_{10}$, and $T_{50}$ of the PVC sample plasticized with DOP (F1) were 226.0, 239.2, and 291.7 °C. The $T_p$, $T_{10}$, and $T_{50}$ were enhanced when DOP was replaced with SOHE, and the $T_p$, $T_{10}$, and $T_{50}$ reached 263.3, 266.8, and 314.3 °C, respectively, when 75% DOP was substituted with SOHE. The $T_p$, $T_{10}$, and $T_{50}$ reached 275.4, 281.8, and 321.8 °C when DOP was fully replaced with SOHE. It can be observed that the thermal stability of PVC samples was increased when the content of SOHE increased. The reason can be explained with the fact that the carbonyl groups and long alkane chains with high heat resistance are contained in the chemical structure of SOHE. The results show that the addition of SOHE can more effectively improve the thermal stability of the PVC matrix than DOP.

2.3. Dynamic Mechanical Analysis. A DMA instrument was used to evaluate the dynamic mechanical property. Figure 6 shows the loss factor of the PVC samples. All the curves show a single peak of tan δ, which indicate that the blends are completely inter soluble and homogeneous materials. The glass transition temperature ($T_g$) is the temperature at the maximum of the tan δ curve, which is an important metric of plasticizing efficiency. As shown in Table 1, the $T_g$ values for F1−F5 are 41.46, 45.68, 46.82, 51.57, and 61.89 °C, respectively. However, the $T_g$ of plasticized PVC samples was much less than the value of 92.3 °C for pure PVC. When 25% and 50% DOP was replaced with SOHE, the $T_g$ was slightly higher than that of pure DOP. With the addition of SOHE, tan δ peaks moved to higher temperatures, and the corresponding $T_g$ values increased. This might be due to the chemical structure of SOHE. Compared with DOP, SOHE has the higher molecular weight, which makes the plasticizing effect reduced when DOP is substituted with SOHE. However, the damping capability increased with the addition of SOHE, leading to taller and narrower peaks than those of sample F1. In addition, the plasticizing mechanism can be explained according to the molecular features of PVC and plasticizers. As indicated in Figure 7, the ester polar groups of SOHE interact with the $\alpha$ hydrogen of PVC chains to form hydrogen bonds, which decreased the interaction of PVC−PVC sites and increased the space between polymer molecules. Furthermore, more free volume in the polymer will be created by the motion of long alkyl chains of SOHE. The interaction promoted the random motion of PVC to make plasticized PVC chains easy to proceed and show flexibility.

2.4. Mechanical Properties. The results of tensile strength and elongation at break of PVC samples before and after heat aging are demonstrated in Figure 8. Compared with F1, PVC plasticized with SOHE (films F2 and F3) had an increased elongation at break and lower tensile strength. Because more dendritic structures with ester carbonyl polar groups and flexible long alkane chains present synergistic plasticizing effects on PVC, SOHE had a remarkable effect on the flexibility when partly replacing DOP. However, the elongation at break decreased and the tensile strength increased when the concentration of SOHE increased to 75 and 100%, respectively. This is mainly because of the high molecular weight of SOHE. These results suggest that SOHE can be used as a secondary plasticizer, endowing the PVC matrix with better flexibility. On the other hand, sample F0 showed the max change of mechanical properties after heat aging. The PVC films plasticized with SOHE as a partial or whole replacement plasticizer for DOP (films F2−F5) did not show much difference in the mechanical properties after aging. The above results suggested that SOHE could improve the thermal stabilities and flexibility of PVC materials.

Figure 6. DMA curves for the PVC samples.

Figure 7. Intermolecular force interaction between SOHE and PVC molecules.
The excellent solvent extraction resistance and volatile resistance makes it more stable than DOP in volatilization experiments. It can be seen that SOHE has excellent heat resistance, which was lower than 1.1% in the experiment of volatilization. However, F1 lost approximately 2.0% of its initial weight. It is similar to that of the extraction test. The weight loss of F3 ranged from 6.3 to 7.9% of their initial weight. The weight loss of F1 is 11.8% of its initial weight loss. This result suggested that SOHE is superior to DOP in solvent extraction resistance. The change of weight loss of PVC samples in the volatilization test is similar to that of the extraction test. The weight loss of F3 was lower than 1.1% in the experiment of volatilization. However, F1 lost approximately 2.0% of its initial weight. It can be seen that SOHE has excellent heat resistance, which makes it more stable than DOP in volatilization experiments. The excellent solvent extraction resistance and volatile resistance of SOHE can be attributed to the high branching degree, large relative molecular mass, and high ester content of SOHE. Compared with DOP, the stronger intermolecular interaction force prevents SOHE migration from PVC blends. It can endow PVC products with long-term stability and safety.

3. CONCLUSIONS

SOHE was synthesized, and we evaluated its effects on mechanical properties, thermal stabilities, and migration stabilities of PVC samples. When SOHE partially or completely substituted commercial plasticizer DOP in soft PVC samples, the effects were investigated. The DMA results suggested that, with the increasing amount of SOHE, the compatibility between the plasticizers and PVC enhanced. TGA was used to examine the thermal stability. The TGA results suggested that SOHE could endow PVC samples with increased thermal stability. When SOHE completely substituted DOP, T_g, T_10, and T_50 increased to 267.5, 275.3, and 338.0 °C, respectively. The tensile results suggested that SOHE had an enhanced plasticizing effect compared with that of DOP. In addition, PVC samples had better migration stability with the substitution of SOHE into DOP. Consequently, this soybean oil-based plasticizer has the potential to be a secondary environmental plastic material.

4. EXPERIMENTAL SECTION

4.1. Materials. Epoxidized soybean oil (98.0%), glycol dimethyl ether (99.5%), methanol (99.5%), glycidyl (98.0%), acetone (99.0%), anhydrous magnesium sulfate (99.5%), acetic anhydride (98.0%), ethyl acetate (98.0%), sodium bicarbonate (99.5%), zinc stearate, and calcium stearate were obtained from Aladdin Chemical Reagent Co., Ltd. (Shanghai, China). PVC (S-1000) was purchased from the Sinopec Qilu Co., Ltd., (Zibo, China).

4.2. Preparation of the Soybean Oil-Based Hyper-branched Polyalcohol (SOL). To a flask equipped with a magnetic stirrer, reflux condenser, and thermometer, epoxidized soybean oil (50 g), methanol (50 g), and four-fluoroboric acid (0.75 g) were mixed at 45 °C for 2 h. Then, the raw product was dissolved in ethyl acetate and distilled water. The oil phase was separated from the water phase. Then, the oil phase was washed with sodium bicarbonate solution and distilled water to neutral. The solvent and water were removed by distillation under vacuum. The SOL was obtained, and the yield was 83.64%.

4.3. Preparation of the Soybean Oil-Based Hyper-branched Polymer (SOH). To a flask equipped with a magnetic stirrer, reflux condenser, and thermometer, epoxidized soybean oil (50 g), methanol (50 g), and four-fluoroboric acid (0.38 g) were dissolved in dimethoxyethane and mixed in a flask under a nitrogen atmosphere. After the mixture was heated to 75 °C, 56 g of glycidol was dropwise added. Then, the mixture was stirred at 100 °C for 4 h. The raw product was dissolved in methanol and acetone. SOH was obtained after vacuum distillation. The yield of SOH was 61.03%.

4.4. Preparation of the Soybean Oil-Based Hyper-branched Ester Plasticizer (SOHE). To a flask equipped with a magnetic stirrer, thermometer, and reflux condenser, SOH (194 g) and acetic anhydride (234 g) were charged. The mixture was heated at 120 °C for 3.5 h. After cooling to room temperature, the raw product was soluble in ethyl acetate and distilled water to neutral. The water was removed through distillation under vacuum. The yield of SOHE was 85.60%.

4.5. Preparation of Plasticized PVC Test Specimens. PVC, thermal stabilizers (Ca salts/Zn salts = 3/1), and plasticizers were compounded in a mixer for 5 min at room temperature. Then, the compound was mixed by double-roller blending rolls (Zhenggong Co., China) at 165 °C for 5 min.
Then, the PVC samples with a thickness of 3 mm were obtained. The formulations were displayed in Table 2.

| component (phr) | F1   | F2   | F3   | F4   | F5   |
|-----------------|------|------|------|------|------|
| total plasticizer content | 40.0 | 40.0 | 40.0 | 40.0 | 40.0 |
| SOE content     | 0.0  | 10.0 | 20.0 | 30.0 | 40.0 |
| DOP content     | 0.0  | 10.0 | 20.0 | 30.0 | 40.0 |
| thermal-stabilizer content | 0.0  | 1.0  | 2.0  | 3.0  | 4.0  |

4.6. Characterizations. 1H NMR spectra in deuterated chloroform (CDCl₃) were recorded on a Bruker ARX 300 spectrometer (Bruker Co., Germany) at 23 °C. Fourier transform infrared (FTIR) spectroscopy was carried out by a Nicolet IS10 spectrometer (Thermo Fisher Scientific Inc., U.S.A.). Dynamic mechanical analysis (DMA) was done in a dual cantilever mode with a frequency of 1 Hz by a DMA Q800 instrument (TA Instruments, New Castle, DE). The heating rate was of 3 °C/min. The testing temperature was swept from −60 to 80 °C. Replicated tests were performed for each specimen to ensure the reproducibility of data. Thermogravimetric analysis (TGA) was conducted in a 409PC thermogravimetric analyzer (Netzsch Co., Germany). Each specimen was scanned from 30 to 600 °C under a nitrogen atmosphere. The heating rate was 10 °C/min. According to ISO 527-2:1993, tensile properties were carried out by a SANS CMT-4303 universal testing machine (Shenzhen Xinsansi Jiliang Instrument Co., China) with a cross-head speed at 10 mm/min. To obtain an average value, five specimens were prepared for each group. Prior to tensile testing, all specimens were conditioned at 23 °C for one day. According to ASTM D1393-98, the extraction tests were carried out. The PVC specimens were sank into petroleum ether at 50 ± 5% relative humidity and 23 ± 1 °C. The extracted specimens were rinsed using flowing water and wiped up after 24 h. Then, the specimens were dried at 30 °C for 24 h in a convection oven (Shanghai Suopu Instrument Co., China). The changes of weight loss before and after sinking were tested. The activated carbon method (ISO 176:2005) was carried out to determine the volatility. The specimens were tested. The activated carbon method (ISO 176:2005) was carried out to determine the volatility. The specimens were placed on the bottom of a metal container. Approximately 120 cm³ of activated carbon was spread over these specimens. The container was placed in the convection oven (Shanghai Suopu Instrument Co., China) for 24 h at a temperature of 70 ± 1 °C. Then, the specimens were dried at 30 °C for 24 h. The specimens were reweighed. The changes of weight loss were measured.

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Notes

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