

Synthesis of Bio-Plasticizer from Soybean Oil and Its Application in Poly(Vinyl Chloride) Films

Xiao Luo^{1,*}, Hongying Chu² and Mengqi Liu¹

¹Henan University of Chinese Medicine, Zhengzhou, 450046, China

²Yellow River Conservancy Technical Institute, Kaifeng, 475004, China

*Corresponding Author: Xiao Luo. Email: lxiao2020@163.com

Received: 15 April 2020; Accepted: 13 May 2020

Abstract: Herein, epoxidized soybean oil methyl ester (ESOM) plasticizer was synthesized for the preparation of plasticized poly(vinyl chloride) (PVC) films by the alcoholysis and epoxidation. The chemical structure of ESOM was investigated by infrared spectrum and ¹H nuclear magnetic resonance. The effect of content of ESOM and petroleum based plasticizer di-2-ethylhexyl phthalate (DEHP) on the performance of plasticized PVC films was studied. The result showed that substituting DEHP with ESOM can improve the thermal stability of plasticized PVC films. When the weight ratio of ESOM and PVC is fixed at 1:2, plasticized PVC film presents higher elongation at break (350.8% vs. 345.1%) and lower tensile strength (14.21 MPa vs. 15.8 MPa) compared with PVC plasticized with DEHP. ESOM showed less weight loss than DEHP in all solvents. The excellent migration resistance of ESOM is helpful to improve stability of plasticized PVC films. In all, the obtained bio-based plasticizer will be potential to replace petroleum based plasticizer DEHP in flexible PVC materials.

Keywords: Soybean oil; epoxy plasticizer; poly(vinyl chloride); glass transition temperature

1 Introduction

Plasticizer, as one of the most important additive, is used to change the plasticity of the polymer materials, make them easy to be processed, and make the polymer product flexible. Plasticizer production capacity around the world is about 8 million tons, and for China is about 4.5 million tons [1]. China has become the world's largest plasticizer producer, consumer and importer. Phthalate esters, such as di-2-ethylhexyl phthalate (DEHP), have always been the dominant market in China, accounting for about 80% [2]. However, phthalate esters have been explicitly banned in electronics, food packing, household products, toys and other industries in the United States, Japan and many European Union countries [3]. The development of new non-toxic plasticizers has become an inevitable trend. Vegetable oil-based plasticizers are a class of non-toxic and environmental friendly plasticizers. At present, researches on vegetable oil-based plasticizers focus on the modification of oils and fats by chemical strategies such as epoxidation, esterification, polymerization, and chlorination to prepare bio-based plasticizers with different structures and properties, and explore the effects of synthetic process and product structure on



This work is licensed under a Creative Commons Attribution 4.0 International License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

the plasticity, precipitation resistance, cold resistance, and thermal stability of poly(vinyl chloride) (PVC) materials, as well as their application in some special materials [4–8].

Bio-based raw materials such as vegetable oil, cardanol, vegetable oil fatty acids, rosin, citric acid, bioglycerin and methyl eleostearate can be synthesized plasticizers with different functional groups [9–13]. Epoxidized soybean oil has been commercialized and used in varieties of environmental protection of PVC products as no-toxic plasticizer. Cardanol was used to synthesis highly branched plasticizers, this kind of cardanol based plasticizer has high toxic doses of 5 g/kg [13]. Epoxidized castor oil can be used as co-plasticizer with epoxidized soybean oil to prepare plasticized PVC materials [14]. Vegetable oil fatty acids and citric acid can be used to prepare bio-based plasticizers via simple esterification [15–16]. Vegetable oil such as soybean oil and castor oil were also reported to prepare flame retardant plasticizer combining with different flame retardant groups [17–20].

Bio-based raw materials can be used to synthesis internal plasticizers to completely prevent plasticizer loss. Waste cooking oil was reported to synthesis mannich base of waste cooking oil methyl ester as an internal plasticizer [21]. In addition, hyperbranched polyglycerol [22], mannich base of cardanol butyl ether [23], lutamic acid [24], propargyl ether cardanol and aminated tung oil methyl ester [25–26] were also used as internal plasticizers.

In the present study, soybean oil was used as raw materials to prepare bio-based plasticizer via alcoholysis and epoxidation using peracid as a catalyst for flexible PVC films. The main advantage of the epoxidation is to avoid the use of organic acids such as formic acid, glacial acetic acid and hydrogen peroxide at room temperature. The chemical structure of the soybean oil based plasticizer was characterized. The plasticizing efficiency was investigated by Tg and tensile tests. The thermal stability and resistance to different solvents were detected and compared with DEHP. The plasticizing mechanism was also explored.

2 Experimental

2.1 Materials

Soybean oil, 3-Chloroperoxybenzoic acid, anhydrous methanol, potassium hydroxide, tetrahydrofuran (THF), chloroform, sodium chloride, DEHP, sulfuric acid, dichloromethane (DCM), sodium thiosulfate and anhydrous magnesium sulfate were provided by Aladdin reagent (Shanghai) Co., Ltd. All the chemicals were analytical purity and used without further purification. PVC were provided by Chlor-Alkai Chemical Industry Co., (Shanghai, China).

2.2 Synthesis of Soybean Oil Methyl Ester

Soybean oil (50 g, 0.05 mol), anhydrous methanol (10 g, 0.313 mol) and potassium hydroxide (0.45 g, 0.008 mol) was mixed and stirred at 45°C for 6 h. Then the mixture was neutralized with sulfuric acid solution and washed with distilled water. Soybean oil methyl ester was obtained after removing water via vacuum distillation. Fig. 1 shows the synthetic route of soybean oil methyl ester.

2.3 Synthesis of Epoxidized Soybean Oil Methyl Ester (ESOM)

Soybean oil methyl ester and 3-chloroperoxybenzoic acid was dissolved in DCM at 0°C (mole ratio of double bond and 3-chloroperoxybenzoic acid is 1:1.2). The mixture was stirred for 4 h at room temperature. Then ESOM was purification using alumina column and removing DCM to obtain ESOM. Fig. 1 shows the synthetic route of ESOM.

2.4 Preparation of Plasticized PVC Films

Plasticized PVC films were prepared by dissolving different weight of PVC and plasticizer in THF (as seen from Tab. 1) at room temperature and stirred for 30 min. Then the solutions were poured into Petri dishes and dried at room temperature for 48 h and in oven at 50°C for another 12 h to remove THF.

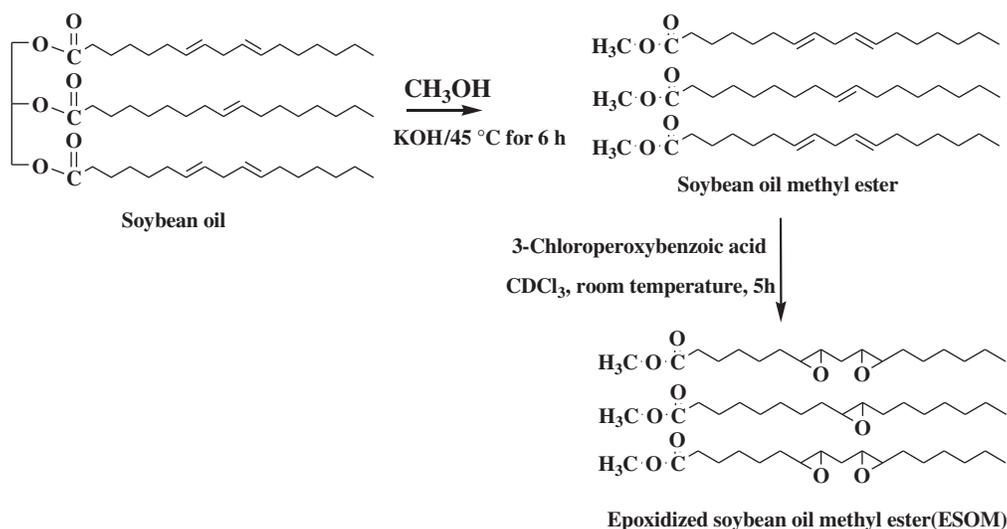


Figure 1: Synthesis of ESOM

Table 1: Formulation of preparing PVC films

Films	PVC (g)	DEHP (g)	ESOM (g)	THF (mL)
PVC	1.0	–	–	30
F1	1.0	–	0.3	30
F2	1.0	–	0.4	30
F3	1.0	–	0.5	30
FD	1.0	0.5	–	30

2.5 Characterization

Chemical structure of the obtained ESOM was characterized with fourier transform infrared (FT-IR) and nuclear magnetic resonance (NMR). The FT-IR spectra of samples were characterized by a Bruker Vertex 70 FT-IR spectrometer equipped with attenuated total reflectance (ATR) accessory. The NMR spectra of ESOM were measured by a Bruker AV300 spectrometer. The shift of infrared spectrum of ester group from ESOM in plasticized PVC films was also detected via FTIR. The thermal stability of plasticized PVC was investigated via a TA TGA550 thermal analyzer. The temperature was heated from room temperature to 600°C with a rate of 10 °C/min under nitrogen. The glass transition temperature (T_g) of PVC films was investigated using a NETZSCH differential scanning calorimeter (DSC) 200 PC analyzer under N_2 atmosphere. The temperature ranged from -40 to 120°C at a heating of $10^\circ\text{C}/\text{min}$. Tensile properties was measured by a CMT4000 universal testing machine with stretching rate of $20\text{ mm}/\text{min}$ at 50% humidity and room temperature. Solvent resistance of plasticized PVC films was investigated according to the related papers [17–18]. Distilled water, 10% (v/v) ethanol, 30% (w/v) acetic acid, olive oil and petroleum ether was used as solvents. The weight loss (WL) was calculated according to the Eq. (1).

$$WL = \frac{W_1 - W_2}{W_1} \times 100 \quad (1)$$

where W_1 was initial weight of samples, and W_2 was final weight of samples.

3 Results and Discussion

3.1 Characterization of Chemical Structure of ESOM

The FT-IR spectra of soybean oil, soybean oil methyl ester and ESOM were shown in Fig. 2. As seen from the FT-IR spectrum of soybean oil, the peaks at 3010, 2925, 2850, 1740, 1160 and 995 cm^{-1} are corresponded to $\text{CH}-\text{C}=\text{}$, $=\text{C}-\text{H}$, $-\text{C}-\text{H}$, $\text{C}=\text{O}$ and $\text{C}-\text{C}$ bonds [27–28]. Absorption peaks in the FT-IR spectra of soybean oil methyl ester presented similar absorption patterns comparing with soybean oil. The reason is that the same type of chemical bonds such as $\text{C}=\text{C}$, $=\text{C}-\text{H}$, $-\text{C}-\text{H}$, $\text{C}=\text{O}$ and $\text{C}-\text{C}$ bonds are in the chemical structure of soybean oil methyl ester. As seen from the FT-IR of ESOM, no $\text{CH}-\text{C}=\text{}$ peak can be found at 3010 cm^{-1} [27]. The results show that there is not $\text{CH}-\text{C}=\text{}$ in the chemical structure of ESOM.

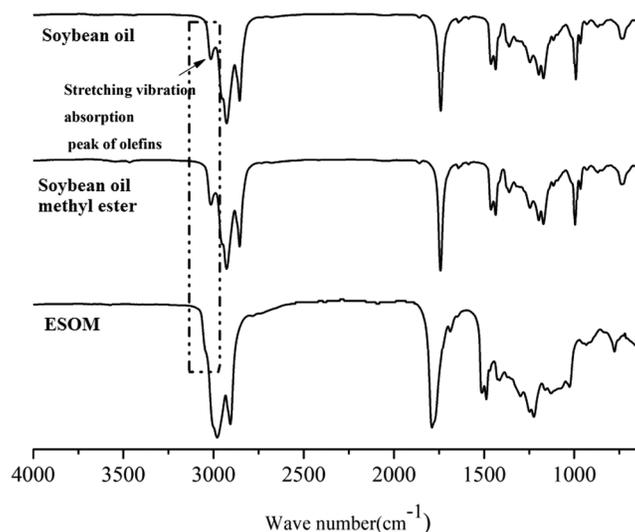


Figure 2: FT-IR of soybean oil, soybean oil methyl ester and ESOM

In order to further investigate the chemical structure of ESOM, ^1H NMR of soybean oil, soybean oil methyl ester and ESOM was detected, Fig. 3 shows the ^1H NMR all reactants and ESOM. As seen from the ^1H NMR of soybean oil, the strong peak at 5.36 ppm is assigned to the protons of double bonds, the peaks at around 4.28–4.42 ppm were corresponded to protons of methyl group and methylene group [29–30]. Comparing with the ^1H NMR spectrum of soybean oil, a new signal appeared at 3.69 ppm in the ^1H NMR spectrum of soybean oil methyl ester, which was assigned to the protons of methyl group connecting to carbonyl groups. The peaks attributing to the methylene group and methylene group from glyceride groups cannot be observed at around 4.28–4.42 ppm, which illustrated that the alcoholysis reaction was finished [29–31]. As seen from the ^1H NMR of ESOM, no any peaks can be found at around 5.36 ppm, and the characteristic absorption peak of proton in epoxy group appears at 2.93 and 3.35 ppm, which indicated that ESOM was obtained.

3.2 Performance of Plasticized PVC Films

The thermal stability of PVC films plasticized with ESOM was detected and compared with DEHP. As seen from Fig. 4, PVC is not thermal stable due to its structural defects. The first thermal degradation process of all plasticized PVC is at around 200–350°C, which is attributed the dehydrochlorination of PVC and degradation of DEHP and ESOM [32–33]. At this stage, it can be found the addition of plasticizer is adverse to enhance thermal stability of plasticized PVC films. However, the thermal stability of PVC plasticized with ESOM is better than DEHP, which is attributed to the higher heat resistance of ESOM

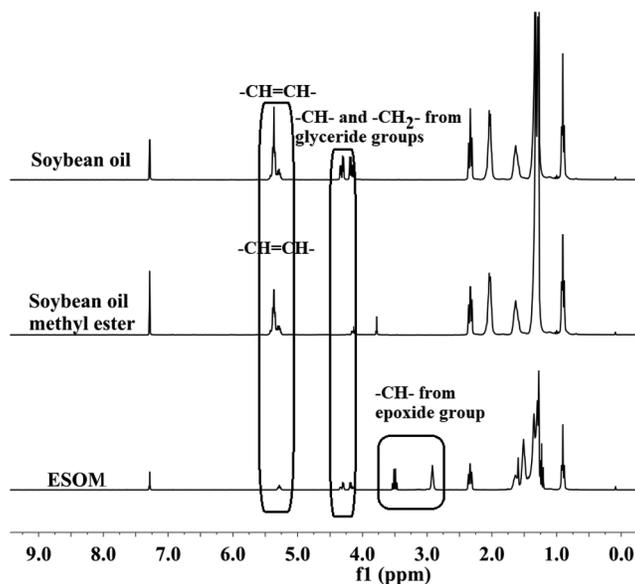


Figure 3: ^1H NMR of soybean oil, soybean oil methyl ester and ESOM

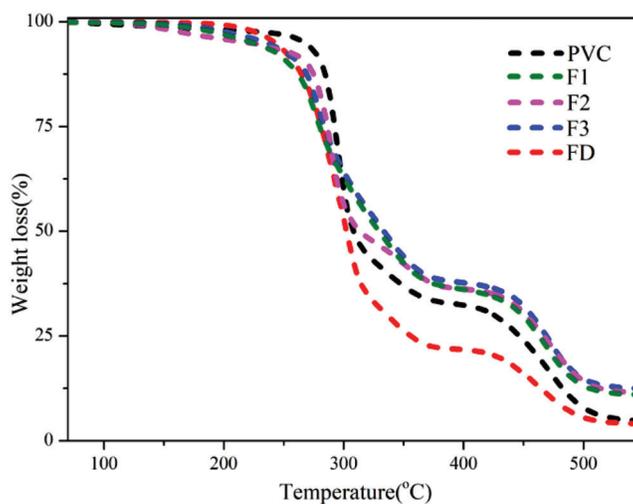


Figure 4: TGA curves of plasticized PVC films

than DEHP. The dechlorination ranges from 350 to 600°C. Thermal stability of PVC films increased with more ESOM adding into the PVC system. Hence, substituting DEHP with ESOM can improve the thermal stability of plasticized PVC films.

In this study, DSC was employed to investigate the T_g of PVC and plasticized PVC films. Fig. 5 shows the DSC curves of PVC and PVC plasticized with ESOM and DEHP. T_g value for PVC films is 89°C. T_g of PVC films plasticized with ESOM(F3) and DEHP(FD) is 24°C and 28°C respectively. Only one endothermic peak for all PVC samples can be found in the DSC curves, which illustrated that ESOM and DEHP are all compatible with PVC [34]. The plasticizing efficiency of ESOM and DEHP were calculated according to Eq. (2).

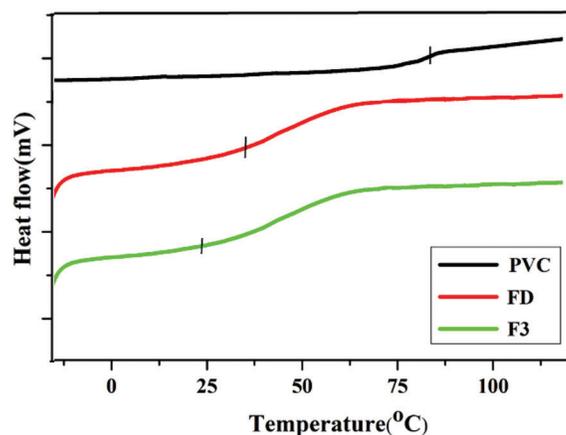


Figure 5: DSC curves of plasticized PVC films

$$E_{\Delta T_g}(\%) = \frac{\Delta T_{g,plasticizer}}{\Delta T_{g,DEHP}} \times 100 \quad (2)$$

where $E_{\Delta T_g}$ is the plasticizing efficiency, and ΔT_g represents the reduction in T_g from PVC to plasticized PVC. $E_{\Delta T_g}$ of ESOM is 73%, which is higher than DEHP (68%), indicating that the plasticizing efficiency of ESOM is better than DEHP.

FT-IR analysis of PVC films was detected and used to investigate the interaction between PVC and plasticizer. As shown in Fig. 6, carbonyl groups of PVC films plasticized with ESOM and DEHO shift to the lower wave number comparing with ESOM and DEHP. The red shift of carbonyl groups indicates that dipole-dipole interaction between ESOM and PVC as well as DEHP and PVC occurred.

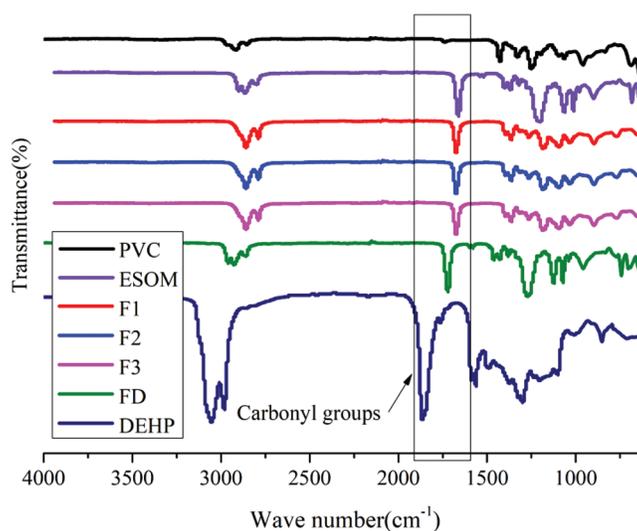


Figure 6: The shift of infrared spectrum of ester group from ESOM in plasticized PVC films

The migration stability of the PVC films was investigated by the extraction tests. The results are showed in Fig. 7. It was obviously found that the weight for plasticized PVC films decreased with more addition of ESOM in all different solvents. The migration resistance in all solvents followed the order of F3 > F2 > F1.

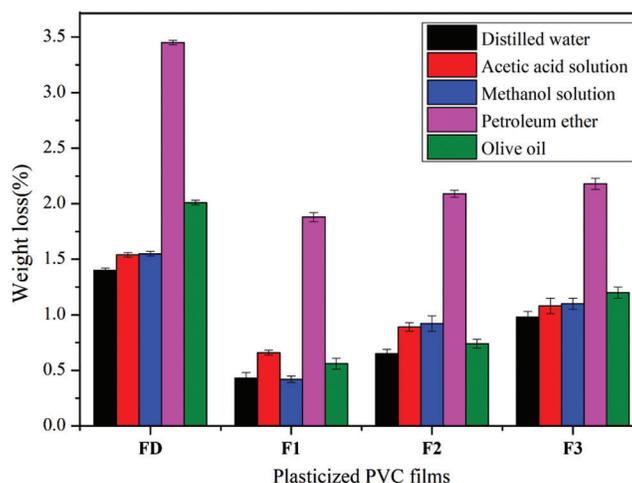


Figure 7: Solvent extraction resistance of plasticized PVC films

However, when plasticized PVC films contained same weight of ESOM and DEHP, F3 showed less weight loss than FD in all solvents. Because the migration stability was related to the chemical structure and functional groups of plasticizers. The polar groups such as ester groups and epoxy group in ESOM molecule may play more strong interaction force with PVC than DEHP.

Tensile test results are summarized in [Tab. 2](#). As seen from [Tab. 2](#), elongation at break of all plasticized PVC films increased with addition of DEHP and ESOM, and tensile strength decreased with addition of DEHP and/or ESOM. For PVC plasticized with ESOM, elongation at break increased from 120.2% to 350.8%, and the tensile strength decreased from 42.1 MPa to 14.21 MPa. When PVC plasticized with the same weight of DEHP, the elongation at break of FD is 345.1%, which is lower than F3. The tensile strength of FD is 15.8 MPa, which is lower than F3. All of the tensile test results indicated that plasticizing effect of ESOM on PVC is more excellent than DEHP.

Table 2: Tensile tests of plasticized PVC films

PVC films	Elongation at break (%)	Tensile strength (MPa)
PVC	120.2 ± 2.0	42.1 ± 0.5
F1	260.2 ± 2.6	28.2 ± 1.1
F2	305.1 ± 3.8	23.7 ± 2.8
F3	350.8 ± 1.9	14.2 ± 1.8
FD	345.1 ± 4.9	15.8 ± 2.1

The plasticizing mechanism can be explored according to the interaction between polar groups (ester group and epoxy group) of plasticizers with hydrogen of PVC chains. The interaction will have effect on increasing decreasing the interaction force between PVC chains [35], as seen from [Fig. 8](#), the addition of ESOM will create free volume in the PVC chains [36]. In addition, ESOP has more epoxy ring structure than DEHP, which may have stronger interaction with hydrogen of PVC chains than DEHP, which will also have effect on decreasing the interaction between PVC chains. Lubricity theory can be used to investigate the plasticizing process [37–38]. Polar groups of the ESOM are strongly attracted to hydrogen of PVC. Polar groups of the ESOM in the plasticized PVC materials can be considered as solvent.

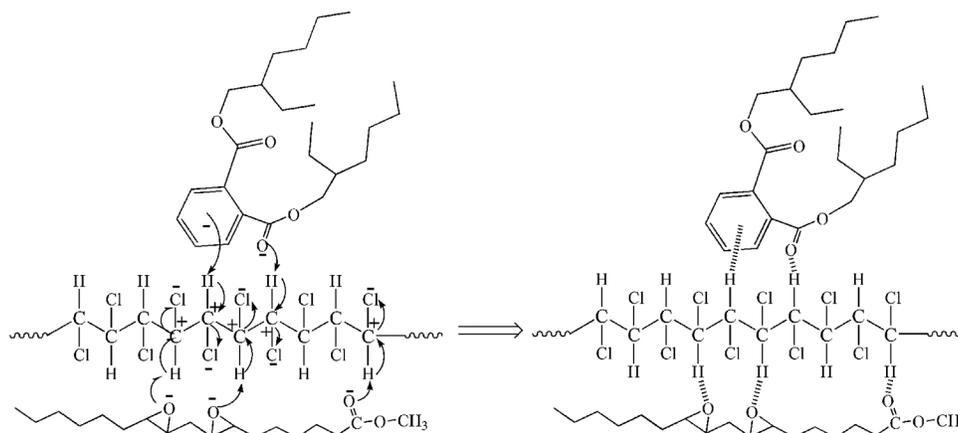


Figure 8: Possible interaction between plasticizer (ESOM and DEHP) and PVC molecules in the plasticized system

Aliphatic hydrocarbon chain of ESOM can be considered as lubricant. Both the solvent and lubricant have effect on promoting the movement of PVC chains.

4 Conclusion

Epoxidized soybean oil methyl ester (ESOM) was successfully synthesized for the flexible PVC films. The resulting ESOM show improved plasticizing effect on PVC and more excellent migration resistance than petroleum based plasticizer DEHP. PVC with the incorporation of ESOM obtains higher elongation at break of 350.8% than PVC films plasticized DEHP. The tensile strength is also decreased from 42.1 MPa of PVC to 14.2 MPa of F3. This may be related to the dipole-dipole interaction between PVC and ESOM, ESOM containing epoxy ring and ester groups may have stronger interaction with hydrogen of PVC chains than benzenes, which will also decrease the interaction between PVC chains and make plasticized PVC films present flexible. In all, the obtained bio-based plasticizer will be potential to replace petroleum based plasticizer DEHP in flexible PVC materials.

Acknowledgement: This work was subsidized for improving medical service and security capacity in 2019 “national survey of traditional Chinese medicine resources” (Financial Society [2019] Number 39).

Funding Statement: This work was subsidized for improving medical service and security capacity in 2019 “national survey of traditional Chinese medicine resources” (Financial Society [2019] Number 39).

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

References

1. Zhang, Y., Wang, P., Wang, L., Sun, G., Zhao, J. et al. (2015). The influence of facility agriculture production on phthalate esters distribution in black soils of northeast China. *Science of the Total Environment*, 506, 118–125. DOI 10.1016/j.scitotenv.2014.10.075.
2. Song, F., Jia, P., Xia, H., Zhang, M., Hu, L. et al. (2019). Rosin-derived poly (vinyl chloride) plasticizer: synthesis, structure, and properties. *Journal of Vinyl and Additive Technology*, 26(2), 180–186. DOI 10.1002/vnl.21731.
3. Zolfaghari, M., Drogui, P., Seyhi, B., Brar, S. K., Buelna, G. et al. (2014). Occurrence, fate and effects of Di (2-ethylhexyl) phthalate in wastewater treatment plants: a review. *Environmental Pollution*, 194, 281–293. DOI 10.1016/j.envpol.2014.07.014.

4. Chieng, B. W., Ibrahim, N. A., Then, Y. Y., Loo, Y. Y. (2017). Epoxidized jatropha oil as a sustainable plasticizer to poly (lactic acid). *Polymers*, 9(6), 204. DOI 10.3390/polym9060204.
5. Kang, H., Li, Y., Gong, M., Guo, Y., Guo, Z. et al. (2018). An environmentally sustainable plasticizer toughened polylactide. *RSC Advances*, 8(21), 11643–11651. DOI 10.1039/C7RA13448G.
6. Jia, P., Hu, L., Feng, G., Bo, C., Zhang, M. et al. (2017). PVC materials without migration obtained by chemical modification of azide-functionalized PVC and triethyl citrate plasticizer. *Materials Chemistry and Physics*, 190, 25–30. DOI 10.1016/j.matchemphys.2016.12.072.
7. Hosney, H., Nadiem, B., Ashour, I., Mustafa, I., El-Shibiny, A. (2018). Epoxidized vegetable oil and bio-based materials as PVC plasticizer. *Journal of Applied Polymer Science*, 135(20), 46270. DOI 10.1002/app.46270.
8. Jia, P., Zhang, M., Hu, L., Feng, G., Bo, C. et al. (2015). Synthesis and application of environmental castor oil based polyol ester plasticizers for poly (vinyl chloride). *ACS Sustainable Chemistry & Engineering*, 3(9), 2187–2193. DOI 10.1021/acssuschemeng.5b00449.
9. Jia, P., Zhang, M., Liu, C., Hu, L., Feng, G. et al. (2015). Effect of chlorinated phosphate ester based on castor oil on thermal degradation of poly (vinyl chloride) blends and its flame retardant mechanism as secondary plasticizer. *RSC Advances*, 5(51), 41169–41178. DOI 10.1039/C5RA05784A.
10. Chen, J., Li, X., Wang, Y., Li, K., Huang, J. et al. (2016). Synthesis and application of a novel environmental plasticizer based on cardanol for poly (vinyl chloride). *Journal of the Taiwan Institute of Chemical Engineers*, 65, 488–497. DOI 10.1016/j.jtice.2016.05.025.
11. Chen, J., Liu, Z., Nie, X., Jiang, J. (2018). Synthesis and application of a novel environmental C26 diglycidyl ester plasticizer based on castor oil for poly(vinyl chloride). *Journal of Materials Science*, 53(12), 8909–8920. DOI 10.1007/s10853-018-2206-7.
12. Li, K., Nie, X., Jiang, J. (2020). Plasticizing effect of epoxidized fatty acid ester and a math model of plasticizer. *Journal of Biobased Materials and Bioenergy*, 14(1), 9–19. DOI 10.1166/jbmb.2020.1930.
13. Ma, Y., Song, F., Hu, Y., Kong, Q., Liu, C. et al. (2020). Highly branched and nontoxic plasticizers based on natural cashew shell oil by a facile and sustainable way. *Journal of Cleaner Production*, 252, 119597. DOI 10.1016/j.jclepro.2019.119597.
14. Thirupathiah, G., Satapathy, S., Palanisamy, A. (2019). Studies on epoxidised castor oil as co-plasticizer with epoxidised soyabean oil for PVC processing. *Journal of Renewable Materials*, 7(8), 775–785. DOI 10.32604/jrm.2019.06399.
15. Gama, N., Santos, R., Godinho, B., Silva, R., Ferreira, A. (2019). Methyl acetyl ricinoleate as polyvinyl chloride plasticizer. *Journal of Polymers and the Environment*, 27(4), 703–709. DOI 10.1007/s10924-019-01383-5.
16. Gama, N., Santos, R., Godinho, B., Silva, R., Ferreira, A. (2019). Triacetin as a secondary PVC plasticizer. *Journal of Polymers and the Environment*, 27(6), 1294–1301. DOI 10.1007/s10924-019-01432-z.
17. Jia, P., Hu, L., Zhang, M., Feng, G., Zhou, Y. (2017). Phosphorus containing castor oil based derivatives: potential non-migratory flame retardant plasticizer. *European Polymer Journal*, 87, 209–220. DOI 10.1016/j.eurpolymj.2016.12.023.
18. Jia, P., Hu, L., Feng, G., Bo, C., Zhou, J. et al. (2017). Design and synthesis of a castor oil based plasticizer containing THEIC and diethyl phosphate groups for the preparation of flame-retardant PVC materials. *RSC Advances*, 7(2), 897–903. DOI 10.1039/C6RA25014A.
19. Chang, B. P., Thakur, S., Mohanty, A. K., Misra, M. (2019). Novel sustainable biobased flame retardant from functionalized vegetable oil for enhanced flame retardancy of engineering plastic. *Scientific Reports*, 9(1), 1–14. DOI 10.1038/s41598-018-37186-2.
20. Wang, F., Pan, S., Zhang, P., Fan, H., Chen, Y. et al. (2018). Synthesis and application of phosphorus-containing flame retardant plasticizer for polyvinyl chloride. *Fibers and Polymers*, 19(5), 1057–1063. DOI 10.1007/s12221-018-7493-8.
21. Jia, P., Zhang, M., Hu, L., Song, F., Feng, G. et al. (2018). A strategy for nonmigrating plasticized PVC modified with mannich base of waste cooking oil methyl ester. *Scientific Reports*, 8(1), 1–8. DOI 10.1038/s41598-017-17765-5.

22. Lee, K. W., Chung, J. W., Kwak, S. Y. (2016). Structurally enhanced self-plasticization of poly (vinyl chloride) via click grafting of hyperbranched polyglycerol. *Macromolecular Rapid Communications*, 37(24), 2045–2051. DOI 10.1002/marc.201600533.
23. Jia, P., Hu, L., Shang, Q., Wang, R., Zhang, M. et al. (2017). Self-plasticization of PVC materials via chemical modification of mannich base of cardanol butyl ether. *ACS Sustainable Chemistry & Engineering*, 5(8), 6665–6673. DOI 10.1021/acssuschemeng.7b00900.
24. Li, L., Tek, A. T., Wojtecki, R. J., Braslau, R. (2019). Internal plasticization of poly(vinyl) chloride using glutamic acid as a branched linker to incorporate four plasticizers per anchor point. *Journal of Polymer Science Part A: Polymer Chemistry*, 57(17), 1821–1835. DOI 10.1002/pola.29455.
25. Jia, P., Zhang, M., Hu, L., Wang, R., Sun, C. et al. (2017). Cardanol groups grafted on poly(vinyl chloride)-synthesis, performance and plasticization mechanism. *Polymers*, 9(11), 621. DOI 10.3390/polym9110621.
26. Jia, P., Hu, L., Yang, X., Zhang, M., Shang, Q. et al. (2017). Internally plasticized PVC materials via covalent attachment of aminated tung oil methyl ester. *RSC Advances*, 7(48), 30101–30108. DOI 10.1039/C7RA04386D.
27. Datta, J., Głowińska, E. (2014). Effect of hydroxylated soybean oil and bio-based propanediol on the structure and thermal properties of synthesized bio-polyurethanes. *Industrial Crops and Products*, 61, 84–91. DOI 10.1016/j.indcrop.2014.06.050.
28. Kulkarni, M., Radhakrishnan, S., Samarth, N., Mahanwar, P. (2018). Stabilization studies of epoxidized soybean oil plasticized PVC films in the presence of beta-diketone. *Advances in Polymer Sciences and Technology: Select Papers from APA 2017, 97, San Diego, California, USA*.
29. Wang, Z., Yuan, L., Ganewatta, M. S., Lamm, M. E., Rahman, M. A. et al. (2017). Plant oil-derived epoxy polymers toward sustainable biobased thermosets. *Macromolecular Rapid Communications*, 38(11), 1700009. DOI 10.1002/marc.201700009.
30. Yuan, L., Zhang, Y., Wang, Z., Han, Y., Tang, C. (2018). Plant oil and lignin-derived elastomers via thermal azide-alkyne cycloaddition click chemistry. *ACS Sustainable Chemistry & Engineering*, 7(2), 2593–2601. DOI 10.1021/acssuschemeng.8b05617.
31. Xu, Y., Yuan, L., Wang, Z., Wilbon, P. A., Wang, C. et al. (2016). Lignin and soy oil-derived polymeric biocomposites by “grafting from” RAFT polymerization. *Green Chemistry*, 18(18), 4974–4981. DOI 10.1039/C6GC00859C.
32. Ji, S., Gao, C., Wang, H., Liu, Y., Zhang, D. et al. (2019). Application of a bio-based polyester plasticizer modified by hydrosilicon-hydrogenation reaction in soft PVC films. *Polymers for Advanced Technologies*, 30(4), 1126–1134. DOI 10.1002/pat.4546.
33. Zheng, X. G., Tang, L. H., Zhang, N., Gao, Q. H., Zhang, C. F. et al. (2013). Dehydrochlorination of PVC materials at high temperature. *Energy & Fuels*, 17(4), 896–900. DOI 10.1021/ef020131g.
34. Jia, P., Ma, Y., Song, F., Hu, Y., Zhang, C. et al. (2019). Toxic phthalate-free and highly plasticized polyvinyl chloride materials from non-timber forest resources in plantation. *Reactive and Functional Polymers*, 144, 104363. DOI 10.1016/j.reactfunctpolym.2019.104363.
35. Jia, P., Ma, Y., Zhang, M., Hu, L., Zhou, Y. (2019). Designing rosin-based plasticizers: effect of differently branched chains on plasticization performance and solvent resistance of flexible poly(vinyl chloride) films. *ACS Omega*, 4(2), 3178–3187. DOI 10.1021/acsomega.8b03612.
36. Chen, J., Liu, Z., Li, X., Liu, P., Jiang, J. et al. (2016). Thermal behavior of epoxidized cardanol diethyl phosphate as novel renewable plasticizer for poly(vinyl chloride). *Polymer Degradation and Stability*, 126, 58–64. DOI 10.1016/j.polymerdegradstab.2016.01.018.
37. Daniels, P. H. (2009). A brief overview of theories of PVC plasticization and methods used to evaluate PVC-plasticizer interaction. *Journal of Vinyl and Additive Technology*, 15(4), 219–223. DOI 10.1002/vnl.20211.
38. Stickney, P. B., Cheyney, L. V. E. (1948). Plasticizers for rubbers and resins. *Journal of Polymer Science*, 3(2), 1–245. DOI 10.1002/pol.1948.120030210.