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Synthesis of a polyester plasticizer from rubber seed oil for polyvinyl chloride

Huabei Li[1, 2 *], Xiaolin Wang[3], Hongying Chu[1, 2], Xinding Yao[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: lihuabei0212@sina.com*

A polyester plasticizer (RSOP) for polyvinyl chloride based on rubber seed oil (RSO) was synthesized. Firstly, RSO monoglyceride were synthesized by the transesterification of RSO with glycerol at 220–240 °C. Secondly, RSOP was synthesized from RSO monoglyceride and adipic acid by esterification. The polyester plasticizer was characterized by GPC, FT-IR, ^{1}H NMR and DSC. Plasticized polyvinyl chloride (PVC) materials with RSOP and dioctyl phthalate (DOP) in varying ratios were prepared via thermal melting process, RSOP was used as a second plasticizer. The properties of the plasticized PVC materials were characterized by a universal testing machine, TGA, DMA and solvent extraction resistance. The obtained PVC materials showed improved thermal stability and lower glass transition temperature than PVC. Solvent extraction resistance and plasticization of plasticized PVC were also improved. This study provides a new strategy for preparing bio-based polyester plasticizer from RSO.

Keywords: Rubber seed oil; polyester; polyvinyl chloride; plasticizer; leaching test.

INTRODUCTION

The work on producing bio-based plasticizer to replace phthalates is a significant challenge in food packing, medical devices, automotive products and storage bags, because recent research work shows that phthalates have adverse impacts on people's health and environment[1–4]. A series of alternative plasticizers such as epoxidized soybean oil, castor oil-based polyester, citrate, vegetable oil-based polyol ester, and tung oil-based hyperbranched ester derived from biomass resources have been widely investigated and applied in polyvinyl chloride(PVC) materials[5–9]. Polyester plasticizers are important additives used in PVC materials. There are many advantages for polyester plasticizers compared phthalate plasticizers, such as improved solvent extraction resistance and thermal stability, low toxic or non-toxic[16]. Recently, many researchers reported nature-based polyester plasticizers derived from oleic acid, citric acid, castor oil, itaconic acid and rice fatty[10–15].

Rubber seed oil(RSO) is a kind of woody vegetable oil extracted from the seeds of rubber trees. The main components of rubber seed oil are palmitic acid, stearic acid, oleic acid, linoleic acid and linolenic acid. It can be used to synthesize a variety of chemicals and polymer materials. Using rubber seed oil to synthesize plasticizer is an important strategy to increase the added value of rubber seed oil. Bio-based plasticizer from RSO can be synthesized via multiple chemical reactions of triglyceride. The polar groups of RSO can improve the compatibility of RSO-based plasticizers and PVC resin. Recent studies have reported that epoxidized rubber seed oil and rubber seed oil epoxy fatty acid methyl ester were synthesized from rubber seed oil and used as plasticizer for PVC and polylactic acid[16].

The purpose of this work was to synthesize a novel polyester plasticizer using RSO, glycerol and adipic acid as raw materials by transesterification, esterification and polycondensation. RSO-based polyester (RSOP) was used as the main plasticizer for PVC to produce medium-scale samples for characterization. The properties of plasticized PVC with RSOP and DOP were studied.

EXPERIMENTAL SECTION

Materials

Adipic acid (AA), DOP, glycerin, calcium stearate, hermal stabilizers and tetrabutyl titanate(TBT) were supplied by Nanning Reagent Co., China. PVC was supplied by Gulf Chemical Co., Ltd . RSO was purchased from Arowana Group Ltd., China.

Synthesis of RSO monoglyceride

The process of the reaction is shown in Figure 1. Glycerol (184 g, 2 mol) was heated at 220–230 °C for 2 h in N_2 atmosphere. RSO (900 g, 1.06 mol) was gradually added in the reaction for 1h. The mixture was stirred for 5.5 h at 230–240 °C. Then the flask was cooled down to room temperature. RSO monoglyceride was obtained after removing excess glycerol by washing with water and distillation[17–18].

Synthesis of RSOP

Monoglyceride (300 g, 0.83 mol), adipic acid (146 g, 1 mol) and TBT (0.14 g, 0.42 mmol) were placed in a round bottom flask. The mixture was heated to melt in N_2 atmosphere. The mixture was stirred at 220–230 °C for 6–8 h to finish esterification. The product was obtained after dissolving in acetone, washing from water and drying. RSOP samples obtained at 6, 8 and 10 h were labeled with RSOP-1, RSOP-2 and RSOP-3. The process of the reaction was shown in Figure 1.

Preparation of PVC materials

Plasticized PVC materials were prepared via thermoplastic blending at 165 °C for 5 min. The formulations are shown in Table 1.

Characterization

The intrinsic viscosities of RSOP were measured with NDJ-1 rotary viscometer. Chemical structures of RSOP

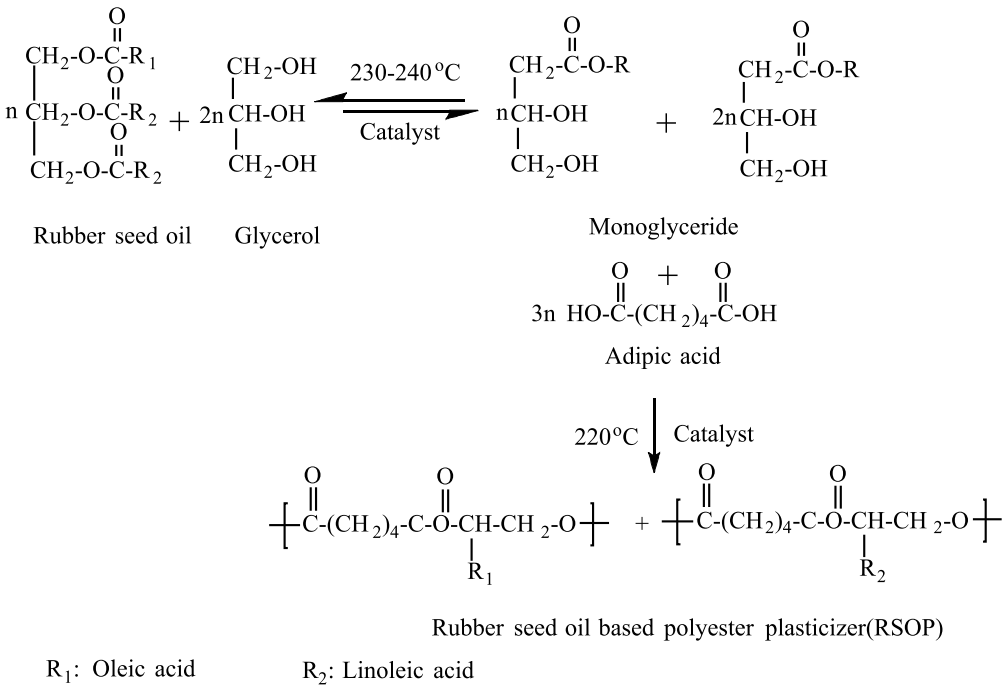


Figure 1. Synthesis of RSOP

Table 1. Formulations of PVC materials

Formulation	PVC/20wt% RSOP-3	PVC/30wt% RSOP-3	PVC/40wt% RSOP-3
PVC (g)	100	100	100
DOP (g)	30	20	10
RSOP-3 (g)	20	30	40
Thermal stabilizers (g)	2	2	2

were studied with AV500 NMR spectrometer and Nicolet iS10 FT-IR. The molecular weights were determined by gel permeation chromatography Model 1515 GPC. TGA was carried out in a TG209F1 TGA thermal analysis instrument (heating rate: 10 °C /min. Temperature range: ambient temperature to 600 °C. DMA was performed via a DMTA Q800 (temperature range: –100 – 100 °C; heating rate: 3 °C/min). The mechanical property was determined using E43.104 Universal Testing Machine. The leaching tests of plasticizers were tested according to the recent papers[19–22].

RESULTS AND DISCUSSION

The GPC results and viscosity of the RSOP are shown in Table 2. When the reaction time increased from 6 to 10 h, Mn increased from 18700 to 22200 g/mol, Mw increased from 18500 to 23500 g/mol, and viscosity increased from 2.2 to 2.9 Pa·s.

The obtained FT-IR curves of RSO, monoglyceride and RSOP are shown in Figure 2. The -CH_3 and -CH_2CH_3 on the fatty acid chains (around 2923 and 2853 cm^{-1}), and the -C=O (1740 cm^{-1}) can be observed in the FTIR of RSO. The -OH (3387 cm^{-1}), -CH_3 and -CH_2CH_3 (2923 and 2851 cm^{-1}), and -C=O (1738 cm^{-1}) can be observed in the spectrum of the monoglyceride[23–26]. The monoglyceride spectra presented a large increase of the absorption band located at 3337 cm^{-1} due to -OH presence in the glycerolysis product. The peak of the -C=O shifted from 1740 cm^{-1} to 1738 cm^{-1}, confirming the occurrence of the glycerolysis reaction. In the spectrum of RSOP, characteristic peaks were also shown: -OH (3466 cm^{-1}), -CH_3 and -CH_2CH_3 (2923 and 2854 cm^{-1}), and -C=O (1738 cm^{-1})[23–26]. The broad -OH at 3466 cm^{-1} in the RSOP samples was observed. The peak at 1045 cm^{-1} decreased because of the disappearance of -OH in the esterification reaction to form -C=O.

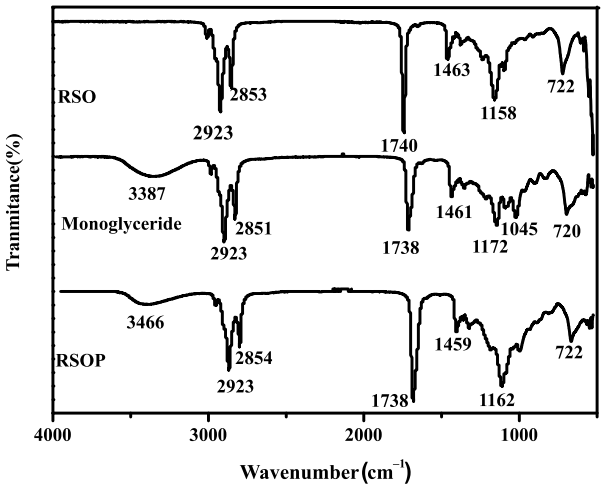


Figure 2. FT-IR of RSO, monoglyceride and RSOP

Figure 3 shows ^{1}H NMR spectra of the RSOP. The peak at around 0.7 ppm was attributed to protons of -CH_3. The integral of this peak should result from three protons per fatty acid chain in monoglyceride. In the spectrum of RSOP, the peak at 1.35 ppm corresponds to the methylene groups of monoglyceride backbones connecting to the ester structure (-CH_2-(CH_2)n-CH_2-).

Table 2. The GPC properties and viscosity of RSOP (25 °C)

Sample	Polycondensation time (h)	Viscosity(Pa·s)	Mn(g/mol)	Mw(g/mol)	Mz(g/mol)
RSOP-1	6	2.2	18700	18500	22400
RSOP-2	8	2.5	20400	21000	23600
RSOP-3	10	2.9	22200	23500	25400

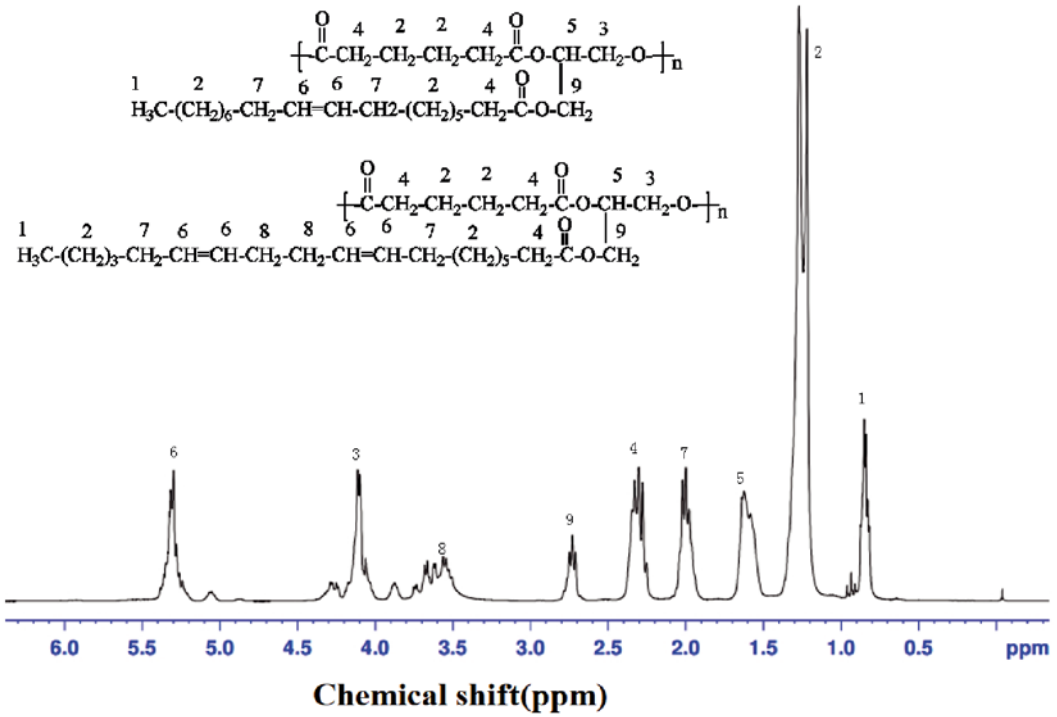


Figure 3. ^{1}H NMR of RSOP

The peaks at 2.0, 2.3 and 2.75 ppm corresponds to the methylene groups of the monoglyceride connecting to -CH_2–CH=CH-CH_2-, -CH_2-(C=O)-O- and -O-CH_2-CH-, respectively[18].

Glass transition temperature (T_g) of RSOP was investigated via DSC (Figure 4). The results showed that T_g of RSOP increased from –53 to –27 °C with the increase of reaction time. There is only one T_g for all RSOPs, which indicated that all RSOPs are homopolymer.

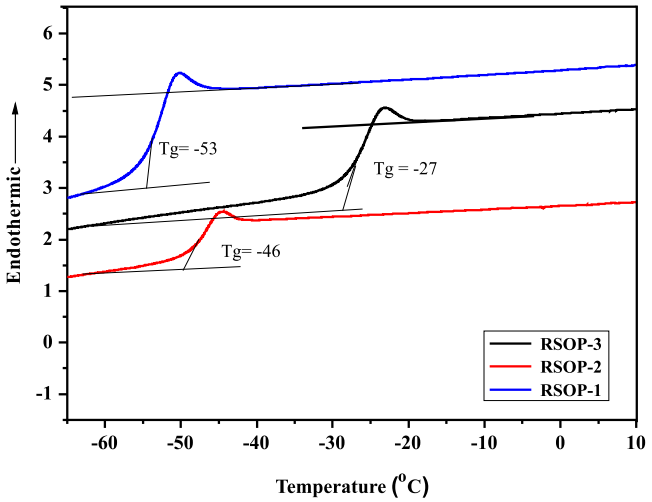


Figure 4. DSC curves of RSOP

Figure 5 shows that torque values changed with mass of plasticizer in PVC materials. When more DOP was replaced with RSOP-3, the torque increased from 12.7 N · m to 19.0 N · m. RSOP-3 with high higher relative molecular weight is more difficult to be fully miscible with PVC than DOP, which caused the increase of torque. The torque increment will cause an increment of melt viscosity, which will increase energy consumption in processing PVC materials.

To determine the effect of RSOP-3 on the thermal stability of the PVC materials, TGA of PVC material

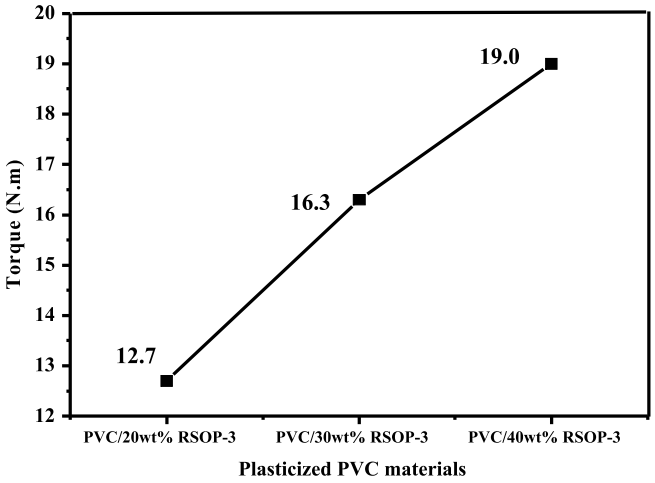


Figure 5. The torque data of plasticized PVC

was investigated (Figures 6 and 7). Table 3 summarizes the TGA and DTG parameters T_d, T_{10} (Temperature at 10% weight loss), T_{50} (Temperature at 50% weight loss), and T_P (Temperature at weight loss peak)). PVC plasticized with RSOP-3 did not lose any weight below

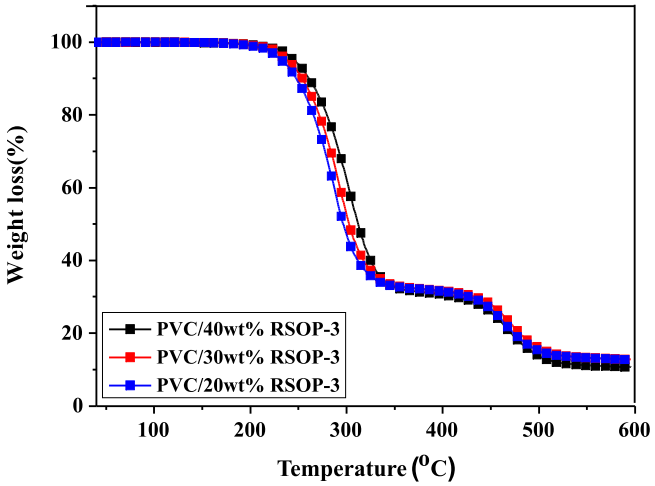


Figure 6. TGA curves of plasticized PVC

Table 3. The thermal properties of PVC materials

Samples	T_d(°C)	T_{10}(°C)	T_{50}(°C)	T_{P1}(°C)	T_{P2}(°C)	T_g(°C)	Char residue(%)
PVC/20wt% RSOP-3	257	261	301	282	458	32	18%
PVC/30wt% RSOP-3	260	263	306	285	459	45	17%
PVC/40wt% RSOP-3	265	266	310	304	461	49	14%

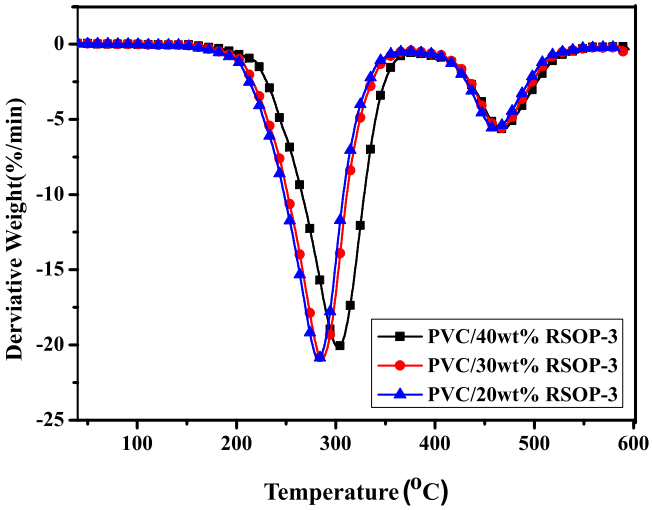


Figure 7. DTG curves of plasticized PVC

200 °C. When the temperature reached 230–380 °C, the high temperature led to dehydrochlorination of PVC[19–21]. Aromatic compounds were formed at above 380 °C. When the quality of RSOP-3 increased in PVC materials, T_d and T_{10} increased (Table 3), but T_{50} and T_p were almost unchanged. The char residue of PVC/20wt% RSOP-3, PVC/30wt% RSOP-3, PVC/40wt% RSOP-3 is 14, 17 and 18% with the addition of RSOP-3 at 600 °C.

T_g of polymeric matrix can be used to evaluate plasticizing effect of plasticizer. T_g derived from DMA and DMA curves are shown in Figure. 8 and Table 3. T_g of PVC/20wt% RSOP-3, PVC/30wt% RSOP-3, PVC/40wt% RSOP-3 were 32, 45 and 49 °C, which indicated all materials are homogeneous systems[19–20]. The increase of T_g indicated that plasticizing efficiency of RSOP-3 is lower than DOP.

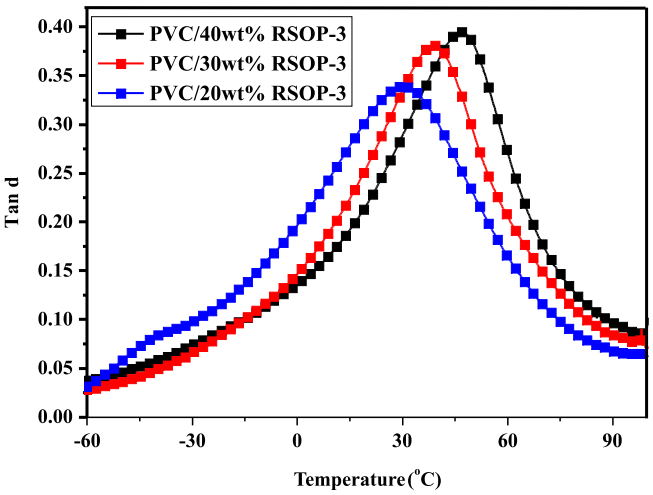


Figure 8. DMA curves of plasticized PVC materials

When more RSOP-3 was added to PVC materials, PVC/40wt% RSOP-3 showed the lowest elongation at break (190%) and the highest tensile strength (27.6 MPa), while PVC/20wt% RSOP-3 showed the highest elongation at break (280%) and the lowest tensile strength (16.2 MPa). The results indicated that plasticizing performance of PVC/20wt% RSOP-3 is more excellent than PVC/40wt% RSOP-3.

When plasticizer (DOP or RSOP-3) and PVC are blended, the small molecules of the plasticizer such as DOP will be inserted between the polymer molecular chains, which will reduce the attraction between the polymer chains and increase the distance between them, the movement of the polymer molecular chains will be increased, and the entanglement between the polymer molecular chains will be reduced, thereby the plasticity of plastics was be improved[27–29]. Therefore, plasticizers with small molecular weight (such as DOP) have stronger plasticizing ability than polyesters (such as RSOP-3).

Table 4. Mechanical properties of PVC materials

PVC materials	Tensile Strength (MPa)	Elongation at Break (%)	Tensile modulus (MPa)
PVC/40wt% RSOP-3	27.6±1.2	190±7	143±3
PVC/30wt% RSOP-3	21.8±1.0	231±5	121±6
PVC/20wt% RSOP-3	16.2±1.3	280±8	94±4

Figure 9 shows the weight loss of plasticized PVC materials with DOP and RSOP-3 in N-hexane, N-hexane can accelerate the migration of plasticizer, and then its migration performance can be evaluated in a short time. With the gradual decrease of DOP and increase of RSOP-3, the weight loss of PVC materials significantly decreased from 7.7 to 3.8%. RSOP-3 showed excellent solvent extraction resistance than DOP, because RSOP-3 with larger relative molecular weight has better migration resistance than DOP.

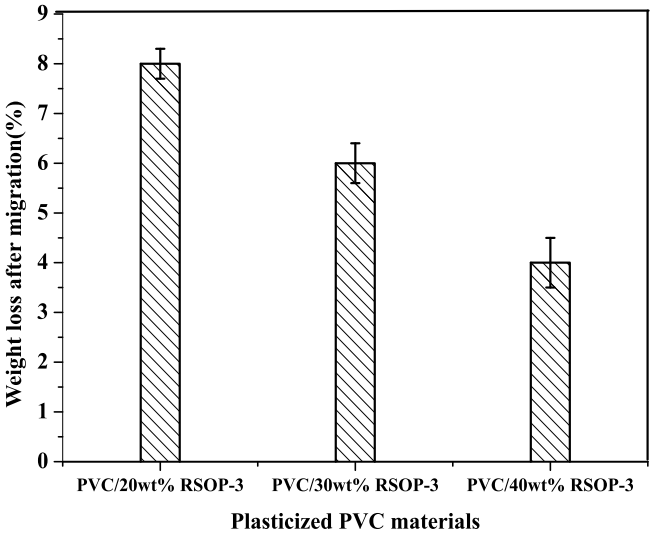


Figure 9. Migration property of RSOP-3

CONCLUSION

A bio-based polyester plasticizer for polyvinyl chloride was synthesized from RSO. When the reaction time increased from 6 to 10 h, Mn of RSOP increased from 18700 to 22200 g/mol, Mw increased from 18500

to 23500 g/mol, and viscosity increased from 2.2 to 2.9 Pa · s. PVC materials plasticized with RSOP-3 and DOP in varying ratios were prepared via the thermal melting process. When more DOP was replaced with RSOP, the torque increased from 12.7 to 19.0 N · m. T_d and T_{10} increased, but T_{50} and T_p were almost unchanged. In addition, RSOP-3 enhanced thermal stability of PVC. The char residue and T_g of PVC/20wt% RSOP-3, PVC/30wt% RSOP-3, PVC/40wt% RSOP-3 is 14, 17 and 18% at 600 °C and 32, 45 and 49 °C. PVC/40wt% RSOP-3 showed the lowest elongation at break (190%) and the highest tensile strength (27.6 MPa). The results indicated that plasticizing efficiency of RSOP-3 is lower than DOP, which is consistent with the DMA results. However, RSOP-3 showed excellent solvent extraction resistance than DOP, because RSOP-3 with larger relative molecular weight has better migration resistance than DOP. This study provides a new strategy for preparing bio-based polyester plasticizer from RSO.

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LITERATURE CITED

1. Abduh, M.Y., Iqbal, M., Picchioni, F., Manurung, R. & Heeres, H.J. (2015). Synthesis and properties of cross-linked polymers from epoxidized rubber seed oil and triethylenetetramine. *J. Appl. Polym. Sci.* 132 (40). DOI: 10.1002/app.42591.

2. Bordes, P., Pollet, E. & Avérous, L. (2009). Nano-biocomposites: Biodegradable polyester/nanoclay systems. *Prog. Polym. Sci.* 34 (2), 125–155. DOI: 10.1016/j.progpolymsci.2008.10.002.

3. Chen, T., Yang, W.J., Li, Y.Y., Chen, X. & Xu, S.Q. (2011). Mono-(2-ethylhexyl) phthalate impairs neurodevelopment: Inhibition of proliferation and promotion of differentiation in PC12 cells. *Toxicol. Lett.* 201 (1), 34–41. DOI: 10.1016/j.toxlet.2010.12.002.

4. Djordjevic, I., Choudhury, N.R., Dutta, N.K. & Kumar, S. (2009). Synthesis and characterization of novel citric acid-based polyester elastomers. *Polymer* 50 (7), 1682–1691. DOI: 10.1016/j.polymer.2009.01.045.

5. Edlund, U. & Albertsson, A.C. (2002). Degradable aliphatic polyesters. *Adv. Polym. Sci.* 157, 67.

6. Feng, G.D., Jia, P.Y., Zhang, L.Q., Hu, L.H., Zhang, M. & Zhou, Y.H. (2015). Synthesis of a novel phosphorus-containing plasticizer based on castor oil and its application for flame retardancy of polyvinyl chloride. *Korean J. Chem. Eng.* 32 (6), 1201–1206. DOI: 10.1007/s11814-014-0288-8.

7. Huang, J., Zhang, J.S., Zhu, G.Q., Yu, X.X., Hu, Y., Shang, Q.Q., Chen, J.Q., Hu, L.H., Zhou, Y.H. & Liu, C.G. (2021). Self-healing, high-performance, and high-biobased-content UV-curable coatings derived from rubber seed oil and itaconic acid. *Prog. Org. Coat.* 159, 106391. DOI: 10.1016/j.porgcoat.2021.106391.

8. Isa, M.T., Ahmed, A.S., Aderemi, B.O., Taib, R.M. & Mohammed-Dabo, I.A. (2013). Effect of fiber type and combinations on the mechanical, physical and thermal stability properties of polyester hybrid composites. *Composites, Part B* 52, 217– 223. DOI: 10.1016/j.compositesb.2013.04.018.

9. Jia, P.Y., Xia, H.Y., Tang, K.H. & Zhou, Y.H. (2018). Plasticizers Derived from Biomass Resources: A Short Review. *Polymers* 10 (12), 1303. DOI: 10.3390/polym10121303.

10. Jia, P.Y., Zheng, M.R., Ma, Y.F., Feng, G.D., Xia, H.Y., Hu, L.H., Zhang, M. & Zhou, Y.H. (2019). Clean synthesis of epoxy plasticizer with quaternary ammonium phosphotungstate as catalyst from a byproduct of cashew nut processing. *J. Cleaner Prod.* 206, 838–849. DOI: 10.1016/j.jclepro.2018.09.238.

11. Kantee, J. & Kajorncheappunngam, S. (2017). Characterization of Epoxidized Rubber Seed Oil. *Key Eng. Mater.* 728, 295–300. DOI: 10.4028/www.scientific.net/KEM.728.295.

12. Kantee, J. & Kajorncheappunngam, S. (2017). Properties of plasticized polylactic acid films with epoxidized rubber seed oil. *Chiang Mai J. Sci.* 44 (4), 1591–1600.

13. Li, Q.G., Shu, X.G., Jia, P.Y. & Zhou, Y.H. (2020). Preparation of Biomass-Based Ester End-Capped Hyperbranched Polys via Facile One-Pot Reaction and Their Performance as Non-Toxic Plasticizers *Polymers* 12 (4), 913. DOI: 10.3390/polym12040913.

14. Liu, C.G., Li, J., Lei, W. & Zhou, Y.H. (2014). Development of biobased unsaturated polyester resin containing highly functionalized castor oil. *Ind. Crops Prod.* 52, 329–337. DOI: 10.1016/j.indcrop.2013.11.010.

15. Ma, Y.F., Song, F., Hu, Y., Kong, Q.Y., Liu, C.G., Rahman, M.A., Zhou, Y.H. & Jia, P.Y. (2020). Highly branched and nontoxic plasticizers based on natural cashew shell oil by a facile and sustainable way. *J. Cleaner Prod.* 252, 119597. DOI: 10.1016/j.jclepro.2019.119597.

16. Ma, Y.F., Song, F., Kong, Q.Y., Li, Q.G., Jia, P.Y. & Zhou, Y.H. (2020). Preparation and Performance of Bio-Based Polyol Ester from One-Pot Synthesis of Castor Oil as Nontoxic Poly(Vinyl Chloride) Plasticizer. *J. Polym. Environ.* 28 (8), 2101–2107. DOI: 10.1007/s10924-020-01754-3.

17. Moffit, J.S., Bryant, B.H., Hall, S.J. & Boekelheide, K. (2007). Dose-dependent effects of sertoli cell toxicants 2,5-hexanedione, carbendazim, and mono-(2-ethylhexyl) phthalate in adult rat testis. *Toxicol. Pathol.* 35 (5), 719–727. DOI: 10.1080/01926230701481931.

18. Montero de Espinosa, L. & Meier, M.A.R. (2011). Plant oils: The perfect renewable resource for polymer science?! *Eur. Polym. J.* 47 (5), 837–852. DOI: 10.1016/j.eurpolymj.2010.11.020.

19. Mosiewicki, M., Aranguren, M.I. & Borrajo, J. (2005). Mechanical properties of linseed oil monoglyceride maleate/styrene copolymers. *J. Appl. Polym. Sci.* 97 (3), 825–836. DOI: 10.1002/app.21790.

20. Okieimen, F.E., Pavithran, C. & Bakare, I.O. (2005). Epoxidation and hydroxlation of rubber seed oil: one-pot multi-step reactions. *Eur. J. Lipid Sci. Technol.* 107 (5), 330–336. DOI: 10.1002/ejlt.200401126.

21. Salimon, J., Omar, T.A. & Salih, N. (2017). An accurate and reliable method for identification and quantification of fatty acids and trans fatty acids in food fats samples using gas chromatography. *Arabian J. Chem.* 10, 1875–1882. DOI: 10.1016/j.arabjc.2013.07.016.

22. Sander, M.M., Nicolau, A., Guzatto, R. & Samios, D. (2012). Plasticiser effect of oleic acid polyester on polyethylene and polypropylene. *Polym. Test.* 31 (8), 1077–1082. DOI: 10.1016/j.polymertesting.2012.08.006.

23. Sathiskumar, P.S. & Madras, G. (2011). Synthesis, characterization, degradation of biodegradable castor oil based polyesters. *Polym. Degrad. Stab.* 96 (9), 1695–1704. DOI: 10.1016/j.polymdegradstab.2011.07.002.

24. Song, F., Huang, C.X., Zhu, X.B., Liu, C.G., Zhou, Y.H. & Jia, P.Y. (2021). Synthesis and application of an environmental epoxy plasticizer with phthalate-like structure based on tung oil and cardanol for poly(vinyl chloride). *J. Appl. Polym. Sci.* 138 (33), 50809. DOI: 10.1002/app.50809.

25. Song, F., Jia, P.Y., Xia, H.Y., Zhang, M., Hu, L.H. & Zhou, Y.H. (2020). Rosin-derived poly(vinyl chloride) plasticizer: Synthesis, structure, and properties. *J. Vinyl Add. Tech.* 26 (2), 180–186. DOI: 10.1002/vnl.21731.

26. Starnes, W.H. (2012). Structural Defects in Poly(vinyl chloride) and the Mechanism of Vinyl Chloride Polymerization: Comments on Recent Studies. *Procedia Chem.* 4, 1-10. DOI: 10.1016/j.proche.2012.06.001.

27. Sudesh, K., Abe, H. & Doi, Y. (2000). Synthesis, structure and properties of polyhydroxyalkanoates: biological polyesters. *Prog. Polym. Sci.* 25 (10), 1503–1555. DOI: 10.1016/S0079-6700(00)00035-6.

28. Vieira, M.G.A., da Silva, M.A., dos Santos, L.O. & Beppu, M.M. (2011). Natural-based plasticizers and biopolymer films: A review. *Eur. Polym. J.* 47 (3), 254–263. DOI: 10.1016/j.eurpolymj.2010.12.011.

29. Wu, Y.M., Xie, Q.W., Gao, C.H., Wang, T. & Wang, C.X. (2014). Synthesis and characterization of a novel aliphatic polyester based on itaconic acid. *Polym. Eng. Sci.* 54 (11), 2515–2521. DOI: 10.1002/pen.23798.