

Synthesis of biomass based plasticizer from linoleic acid and cardanol for preparing durable PVC material

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Research Article

Keywords: Biomass based plasticizer, plasticizing effect, polyvinyl chloride, solvent extraction resistance

Posted Date: April 12th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-381777/v1>

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Version of Record: A version of this preprint was published at Journal of Polymers and the Environment on March 23rd, 2022. See the published version at <https://doi.org/10.1007/s10924-022-02423-3>.

Abstract

In this paper, we synthesized a kind of bio-based plasticizer epoxidized linoleic acid cardanol ester(ELCE) from cardanol and linoleic acid. Its chemical structure was characterized with FT-IR and ^1H NMR. Polyvinyl chloride(PVC) blends plasticized with ELCE were prepared via thermoplastic blending with torque rheometer. The performance including torque, mechanical property, thermal stability, plasticizing property and migration resistance of plasticized PVC blends were investigated and compared with plasticized PVC blends with commercial plasticizer dioctyl phthalate(DOP). The results showed that ELCE improved thermal stability of PVC blends. ELCE played more excellent plasticizing effect on PVC blends than DOP. The better solvent extraction resistance and volatile resistance of ELCE make it impossible to completely replace DOP in PVC products.

1. Introduction

Plasticizers are functional additives added to polymers to improve their flexibility, plasticity, processability and tensile properties, especially widely used in polyvinyl chloride(PVC) products. The addition of plasticizer can weaken the intermolecular secondary bond force, reduce the crystallinity, increase the relative movement of molecular segments, and improve the plasticity of the materials[1–3]. The main effect of plasticizer is to reduce hardness, softening temperature, elastic modulus and embrittlement temperature, and improve flexibility and elongation. According to different chemical structures, the most commonly used plasticizers include carboxylic acid esters, hydrocarbons, phosphorus esters[4–5], ethers, haloalkanes, polyethylene glycol and epoxy compounds[6–8]. Among them, the output and consumption of phthalate plasticizers account for a large proportion in the total production and sales of plasticizers. However, with the enhancement of people's awareness of environmental protection, especially after the discovery of phthalate plasticizers' potential threat to human health and environmental pollution, since the 1990s, the global health requirements for plastic additives have been increasing, Developed countries and regions have issued laws and regulations to restrict the use of this kind of plasticizer.

From the development of modern plasticizer, vegetable oil was the first plasticizer to be used[9–11]. In 1856, Marius in Paris used castor oil as plasticizer of collodion. There are many defects in the direct use of vegetable oil as PVC plasticizer, but through the chemical structure modification of vegetable oil, it can be well used as PVC exothermic plasticizer. Because of its many advantages, its consumption has accounted for about 8% of the total amount of plasticizer. In the United States, its consumption is second only to petroleum products plasticizer, accounting for the third place of consumption. In addition, bio-based plasticizer derived from tributyl citrate[12], castor oil[13], tung oil[14], fatty acid[15], rosin have been widely reported[16]. Internally plasticized PVC materials based on biomass resources such as cardanol, rosin have been also reported, which not only showed flexible property, but also present no plasticizer migration[17–18]

In this paper, we reported a kind of bio-based plasticizer epoxidized linoleic acid cardanol ester(ELCE) from cardanol and linoleic acid. Plasticized PVC blends with ELCE were prepared via thermoplastic

blending with torque rheometer. The plasticizing effect of ELCE on PVC was investigated based on tensile tests, glass transition temperature(T_g) and compatibility between PVC and ELCE. The solvent extraction resistance and plasticizing mechanism was also investigated.

2. Experimental

2.1 Materials

Cardanol, linoleic acid, tetrabutyl titanate, dioctyl phthalate(DOP), phosphoric acid, sodium chloride, tetrahydrofuran, 40wt% hydrogen peroxide solution and dichloromethane were provided by Aladdin Reagent Co., Ltd. PVC with K value 65-68 was obtained from McLean Reagent Co., Ltd .

2.2 Synthesis of linoleic acid cardanol ester

Linoleic acid cardanol ester was synthesized through esterification. The reaction procedure was shown in Figure 1. 10 g (35.71mmol) linoleic acid, 10.78g (35.71mmol) cardanol and 0.62 g tetrabutyl titanate were added into a 250ml three-necked round-bottom flask with a water separator, mechanical stirrer and N_2 inlet pipe. The mixture was heated to 160 °C and kept the temperature until all the reactants melted completely. The temperature was slowly increased to 180 °C and kept the temperature for 4.5 h to finish esterification, then the condensation was allowed to proceed in vacuum at 160 °C until acid value remained unchanged. The resulting esterification products were allowed to cool and dissolved in acetone and reprecipitated from water. The dissolution and reprecipitation were repeated three times and the polyester products were air dried for 36h and finally dried at 60 °C in vacuum for 24 h.

2.3 Synthesis of epoxidized linoleic acid cardanol ester(ELCE)

20g (35.46mmol)linoleic acid cardanol ester, 18g glacial acetic acid and 1.5g phosphate were mixed in a four-necked round-bottom flask which was equipped with a mechanical stirrer, condenser pipe, thermometer and constant pressure funnel. 110 g 40 wt% hydrogen peroxide solution were dropped in the reaction in 30min and stirred at 50°C for 4h to finish epoxidation reaction. The product was subsequently washed with NaCl saturated solution. With the evaporation of water the product was obtained. The epoxy value was 2.21%. Determination of epoxy value was in accordance with the Chinese standards GB/T 1667-2008. The chemical reaction process of ELCE was shown in Figure 1.

2.4 Preparation of plasticized PVC materials

PVC blends were melt process at 165 °C for 5 min at 50 rpm using Poly Lab Torque rheometer (Hakke Insturment Crop., Germany). The PVC resin was pre-treated by drying at 60 °C for 2 h to eliminate possible absorbed water on the surface of particle. Formulations used for preparing plasticized PVC blends were showed in Table 1. Dumbbell-shaped samples of blends were molded on a MiniJetII Micro-injection molding machine (Hakke Insturment Crop., Germany) according GB/T 17037.1-1997 (China). Mounding conditions were set at 165 °C for 5 min at 550 Bar.

Table 1 Composition of PVC blend plasticized with ELCE

Samples	PVC (g)	DOP(g)	ELCE(g)	Thermal stabilizers(g)
P0	100	40	0	2
P1	100	35	5	2
P2	100	30	10	2
P3	100	20	20	2

2.4 Characterization

FTIR spectroscopy was performed on a Nicolet IS 10 IR spectrometer (Nicolet Co., USA) in a range of 4000~500 cm^{-1} and the resolution of 4 cm^{-1} . ^1H NMR spectra were confirmed by a Bruker ARX 300 nuclear magnetic resonance spectrometer with CDCl_3 as the solvent and tetramethylsilane as the internal standard. TGA measurements were performed NETZSCH TG 209F1 (Netzsch Instrument Crop., Germany) in a nitrogen atmosphere was used with a heating rate of 10°C/min and a temperature range of 40-600°C. The DMA was performed via a DMTA Q800 (TA Instruments) with gas cooling accessory to observe the α -transitions of the PVC films under investigation. Rectangular samples of geometry 80 (L) \times 10 (W) \times 4 (T) mm^3 . The oscillatory frequency of the dynamic test was 1 Hz. The temperature was raised at a rate of 3°C/min in the range of -80 to 100°C. The crystal structure of PVC materials was investigated via X-ray diffraction (XRD) with a D8 FOCUS (BRUKER, Germany) operated at 45 kV and 40 mA using Cu-K α radiation with a graphite diffracted beam monochromatic. The patterns were recorded in a 2-theta rang from 0° to 80°. The microstructure of plasticized PVC blends was observed by Leica dm750 optical microscope. Volatility test was according to ISO176:2005 (determination of plasticizer loss of activated carbon determination). Extraction tests were according to ASTM D 1239-98. The PVC blend was immersed in petroleum ether at 23 \pm 1 °C and 50 \pm 5% relative humidity. Tensile properties test was measured by a CMT4000 universal testing machine (according to ISO 527-2: 1993) with stretching rate of 20 mm/min. Each named sample need test at least four times.

Results And Discussion

Chemical structure of ELCE

Chemical structure of ELCE characterized with FTIR and compared with linoleic acid, cardanol and linoleic acid cardanol ester. Figure 2 shows their FTIR. As seen from FT-IR of linoleic acid, the peak at 3006.2 cm^{-1} attributed to =C-H, the strong peak at around 1720 cm^{-1} corresponded to C=O[15]. For the FT-IR of cardanol, the peak at around 3410 cm^{-1} attributed to -OH, and the peaks at 3007.1 cm^{-1} corresponded to =C-H[19-20]. There is no -OH peak at around 3410 cm^{-1} in FT-IR of linoleic acid cardanol ester, which indicated that the esterification was completed. As seen from the FT-IR of ELCE, it cannot be observed any

peak attributing to =C-H at 3000cm^{-1} - 3010cm^{-1} [21], which indicated that the epoxidation reaction was completed and the ELCE was obtained.

Figure 3, Figure 4, Figure 5 and Figure 6 show ^1H NMR of linoleic acid, cardanol, linoleic acid cardanol ester and ELCE. As seen from Figure 3, the peak at 5.2-5.6ppm attributed to protons of -CH=CH-, the peaks at 4.2-4.4ppm attributed to protons of -CH₂- connecting to -CH=CH-. The peak at around 1.3-2.3ppm attributed to protons of other -CH₂-. The peak at 0.9ppm corresponded to protons of -CH₃[15]. As seen from Figure 4, the peaks at around 6.2-7.3ppm attributed to protons of -CH₂ from benzene ring. The peak at 5.5ppm attributed to protons of -CH=CH-. The peaks at around 1.4-2.9ppm corresponded to other protons of -CH₂-. The protons of -CH₃ appeared at 0.9ppm[19-20]. When the esterification was finished, it can be observed that the protons of -CH₂- from benzene ring of cardanol appeared at around 6.9-7.3ppm in the ^1H NMR of linoleic acid cardanol ester, and the protons of -CH=CH- from linoleic acid appeared at 5.4ppm, which indicated that the linoleic acid cardanol ester was obtained. Figure 6 shows the ^1H NMR of ELCE, there was no peak attributing to the protons of -CH=CH- at around 5.4ppm, and the peak corresponding to the protons of -CH₂- connecting to epoxy group appeared at 3.2ppm, which illustrated that ELCE was obtained.

Performance of PVC plasticized with ELCE

Melting behavior of PVC blends was investigated by torque variation during blends mixing in relation to the plasticizer content. Processing data were collected during mixing in the Haake chamber. The torque data were collected during thermoplastic blending process of PVC and plasticizer. The torque values relative to the mass of plasticizer in blends were shown in Figure 7. When the mass of ELCE increased from 0g to 20g, the torque of PVC blends decreased from 20N·m(P0) to 11.2N·m(P3), which corresponds to 44% decrement. The reduction of torque value means that using ELCE to replace DOP will decrease the melt viscosity and improve thermoplastic processing of PVC blends.

Figure 8 and Figure 9 shows the TGA and DTG curve of P0, P1, P2 and P3. It can be observed that there were two degradation stages for all PVC blends, which have been reported that the first degradation stage corresponding to formation and stoichiometric elimination of HCl, and the second degradation stage attributing to cross linking containing C=C bonds[22-23]. In addition, with more ELCE added in PVC blends, the degradation temperature increased, which indicated that ELCE delayed the thermal degradation of plasticized PVC materials. When PVC blends plasticized with same mass of ELCE and DOP, PVC plasticized with EPAE showed more excellent thermal degradation stability. This is mainly because the epoxy group of ELCE can react with HCl, thereby delaying thermal decomposition[24].

DMA is usually used to measure the viscoelasticity of blends, which can show the change of $\tan \delta$ with temperature. The temperature at the maximum of the $\tan \delta$ vs. temperature curve is defined as the glass transition temperature (T_g), which is an important indicator to measure plasticization efficiency. Figure 5 shows the $\tan \delta$ vs. temperature curves of all plasticized PVC samples. All PVC materials show one T_g , which indicated that ELCE and DOP have excellent compatibility with PVC. For P0, the T_g was 55.8°C. When the DOP was replaced with ELCE in PVC blends, T_g decreased from 55.8°C to 36.7°C, which illustrated that ELCE played a more efficient plasticizing effect on PVC than DOP. Because the chlorine atom

on the PVC molecular chain has an electron withdrawing effect, so the hydrogen atom shows electropositivity. The electronegative oxygen atoms in the ester group and epoxy group on ELCE form hydrogen bond interaction with the positive hydrogen atoms on the PVC molecular chain. In addition, the long non-polar alkyl chain of ELCE can play the role of lubrication on the PVC molecular chain, thereby increasing the volume of the amorphous region of the blend, which lead to a decrease in T_g .

Figure 13 shows the XRD diffractograms of plasticized PVC blends, which was used to determine the structure, complexation and crystallization of the PVC matrix. From the corresponding angle of the characteristic peaks and the applying Bragg's Law ($n\lambda=2d\sin\theta$), for λ of 1.542 Å, the interlamellar basal distances (d) could be calculated. The diffractograms showed two characteristic peaks at $2\theta=17.9^\circ$ and 24.8° . According the XRD diffractograms, there was no difference in the crystalline of PVC blends plasticized with ELCE and DOP, which illustrated that both ELCE and DOP did not change the crystallinity of PVC blends.

Microstructure of PVC blends was investigated with optical microscope to reveal the plasticizing mechanism. Figure 12 shows the microstructure of all plasticized PVC blends. For P0, which shows the rough and irregular microstructure and there are many agglomerates on the surface of P0. With more ELCE added into the PVC blends, the microstructure of plasticized PVC materials, as seen from Figure 12 (P1-P3), the rough and irregular microstructure, and agglomerates disappeared gradually. P3 shows homogeneous and smooth surface microstructures, indicating excellent compatibility between PVC and ELCE[25], because the strong interaction of the polar groups of ELCE(ester group, benzene ring and epoxy groups) with polar groups of PVC.

Figure 12 Resistance to volatilization and migration of plasticized PVC blends

Figure 12 shows the mass loss of all plasticized PVC blends after the volatilization resistance test and solvent extraction resistance test. The volatility loss of the plasticized samples P0, P1, P2 and P3 were 5.94%, 3.76%, 1.92% and 0.42%, respectively. Obviously, P3 shows better volatilization resistance than other samples, which indicated that ELCE has excellent migration resistance in PVC, and is greatly superior to DOP. Figure 12 shows the extraction loss of P0, P1,P2 and P3 in extraction tests were according to ASTM D 1239-98. The PVC blend was in petroleum ether at $23 \pm 1^\circ\text{C}$ and $50 \pm 5\%$ relative humidity. For P0, the weight loss was 15.56% of mass, while for P3, the weight loss was 6.74%, which illustrated that ELCE showed excellent solvent extraction resistance than DOP. The polarity and structure of the plasticizer have a decisive influence on the migration resistance and solvent extraction resistance of the plasticizer in PVC. The abundant epoxy groups and higher molecular weight give ELCE stronger intermolecular interactions and higher compatibility with PVC than that of DOP[26-28], thus obtaining more excellent migration stability and volatility in PVC blends.

Table 2 shows tensile strength and elongation at break of all PVC materials. It can be observed from Table 2 that with the increase of the ELCE in PVC blends, the elongation at break of the PVC blends increased from $122.12\pm 6.51\%$ to $250.43\pm 7.12\%$, while the tensile strength and modulus of elasticity gradually decreased. This indicated that the addition of ELCE increased the flexibility and movement

ability of the PVC molecular chain to a certain extent, and the effect becomes more obvious as the content increases. This is because that chemical structure of ELCE is similar to DOP. In addition, the epoxy group in the long aliphatic chain of ELCE has a strong electrostatic interaction with the PVC molecular chain, which can inserted PVC molecular chains and increased free volume of PVC chains[29-30].

Table 2 Tensile data of plasticized PVC materials			
PVC materials	Tensile strength (MPa)	Elongation at break (%)	Modulus of elasticity (MPa)
P0	34.12±0.78	122.12±6.51	193.45±2.18
P1	29.64±0.98	180.89±7.18	156.87±6.12
P2	25.34±0.89	210.45±9.87	143.45±7.01
P3	22.16±0.68	250.43±7.12	129.21±5.12

The plasticizing mechanism can be explained according to formation of hydrogen bonds between PVC and plasticizers, as seen from Figure 13, the ester groups and epoxy groups of ELCE interacted with α -hydrogen of PVC chains to form hydrogen bonds, which decreased interaction of PVC chains and increased the distance between themselves[31-32]. The interaction promoted the movement of PVC chains to make plasticized PVC flexible and malleable.

Conclusions

In summary, a novel biomass based epoxy plasticizer(ELCE) was prepared using cardanol and linoleic acid as raw materials. Performance of PVC plasticized ELCE was investigated. When the mass of ELCE increased from 0g to 20g, the torque of PVC blends decreased from 20N·m(P0) to 11.2N·m(P3), which corresponded to 44% decrement. When PVC blends plasticized with same mass of ELCE and DOP, PVC plasticized with EPAE showed more excellent thermal degradation stability. This is mainly because the epoxy group of ELCE reacted with HCl, thereby delaying thermal decomposition. When the DOP was replaced with ELCE in PVC blends, Tg decreased from 55.8°C to 36.7°C, the elongation at break of the PVC blends increased from 122.12±6.51% to 250.43±7.12%, which illustrated that ELCE played more efficient plasticizing effect on PVC than DOP. The volatility loss of the plasticized samples P0, P1, P2 and P3 was 5.94%, 3.76%, 1.92% and 0.42%, respectively. Obviously, P3 shows better volatilization resistance than other samples than DOP. Therefore, the plasticizer originated from cardanol and linoleic acid is a suitable candidate for plasticizing PVC, with advantages of environmentally benign, guaranteed safety issue, and enhanced performance to the PVC materials.

Declarations

ACKNOWLEDGEMENTS

This work was supported by the Science and technology project of Henan Province (202102310593) and Science and technology project of Kaifeng city(2002003).

References

1. 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.
2. Xuan, W., Hakkarainen, M., & Odelius, K. (2019). Levulinic Acid as a Versatile Building Block for Plasticizer Design. *ACS Sustainable Chemistry & Engineering*, 7(14), 12552-12562.
3. Briou, B., Caillol, S., Robin, J. J., & Lapinte, V. (2019). Non-endocrine disruptor effect for cardanol based plasticizer. *Industrial Crops and Products*, 130, 1-8.
4. Jia, P., Feng, G., Bo, C., Hu, L., Yang, X., Zhang, L., ... & Zhou, Y. (2018). A composition of phosphaphenanthrene groups-containing castor-oil-based phosphate plasticizer for PVC: synthesis, characterization and property. *Journal of Industrial and Engineering Chemistry*, 60, 192-205.
5. Bocqué, M., Lapinte, V., Courault, V., Couve, J., Cassagnau, P., & Robin, J. J. (2018). Phosphonated lipids as primary plasticizers for PVC with improved flame retardancy. *European Journal of Lipid Science and Technology*, 120(8), 1800062.
6. 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.
7. Chen, J., Wang, Y., Huang, J., Li, K., & Nie, X. (2018). Synthesis of tung-oil-based triglycidyl ester plasticizer and its effects on poly (vinyl chloride) soft films. *ACS Sustainable Chemistry & Engineering*, 6(1), 642-651.
8. Song, F., Xia, H., Jia, P., Zhang, M., Hu, L., & Zhou, Y. (2018). The effects of epoxidized acrylated castor oil (EACO) on soft poly (vinyl chloride) films as a main plasticizer. *Polish Journal of Chemical Technology*, 20(4).
9. Greco, A., Ferrari, F., & Maffezzoli, A. (2020). Compression behavior of soft PVC foams obtained by cardanol-derived plasticizer. *Journal of Cellular Plastics*, 56(5), 515-530.
10. Ali, M., Lu, Y., Ahmed, S., Khanal, S., & Xu, S. (2020). Effect of Modified Cardanol as Secondary Plasticizer on Thermal and Mechanical Properties of Soft Polyvinyl Chloride. *ACS omega*, 5(28), 17111-17117.
11. Rouane, A., Zerrouki, D., Aillerie, M., & Henni, A. (2020). Spectroscopic and mechanical properties of PVC plasticized by bio-plasticizer ESO. *Journal of Polymer Research*, 27(1), 1-8.
12. Chaos, A., Sangroniz, A., Gonzalez, A., Iriarte, M., Sarasua, J. R., del Río, J., & Etxeberria, A. (2019). Tributyl citrate as an effective plasticizer for biodegradable polymers: effect of plasticizer on free volume and transport and mechanical properties. *Polymer International*, 68(1), 125-133.
13. Ma, Y., Liao, S., Li, Q., Guan, Q., Jia, P., & Zhou, Y. (2020). Physical and chemical modifications of poly (vinyl chloride) materials to prevent plasticizer migration-Still on the run. *Reactive and Functional*

Polymers, 147, 104458.

14. Jia, P., Ma, Y., Xia, H., Zheng, M., Feng, G., Hu, L., ... & Zhou, Y. (2018). Clean synthesis of epoxidized tung oil derivatives via phase transfer catalyst and thiol–ene reaction: a detailed study. *ACS Sustainable Chemistry & Engineering*, 6(11), 13983-13994.
15. Liu, D., Shen, Y., Jiang, P., Wai, P. T., Zhang, Z., Zhang, P., ... & Zhao, H. (2021). An efficient cold-resistant strategy: synthesis and application of green cold-resistant bio-based plasticizer for poly (vinyl chloride). *European Polymer Journal*, 142, 110154.
16. Song, F., Jia, P., Xia, H., Zhang, M., Hu, L., & Zhou, Y. (2020). Rosin-derived poly (vinyl chloride) plasticizer: Synthesis, structure, and properties. *Journal of Vinyl and Additive Technology*, 26(2), 180-186.
17. Jia, P., Ma, Y., Song, F., Hu, Y., Zhang, C., & Zhou, Y. (2019). Toxic phthalate-free and highly plasticized polyvinyl chloride materials from non-timber forest resources in plantation. *Reactive and Functional Polymers*, 144, 104363.
18. Jia, P., Ma, Y., Feng, G., Hu, L., & Zhou, Y. (2019). High-value utilization of forest resources: Dehydroabietic acid as a chemical platform for producing non-toxic and environment-friendly polymer materials. *Journal of Cleaner Production*, 227, 662-674.
19. Ma, Y., Song, F., Hu, Y., Kong, Q., Liu, C., Rahman, M. A., ... & Jia, P. (2020). Highly branched and nontoxic plasticizers based on natural cashew shell oil by a facile and sustainable way. *Journal of Cleaner Production*, 252, 119597.
20. Jia, P., Zheng, M., Ma, Y., Feng, G., Xia, H., Hu, L., ... & Zhou, Y. (2019). Clean synthesis of epoxy plasticizer with quaternary ammonium phosphotungstate as catalyst from a byproduct of cashew nut processing. *Journal of Cleaner Production*, 206, 838-849.
21. Suzuki, A. H., Botelho, B. G., Oliveira, L. S., & Franca, A. S. (2018). Sustainable synthesis of epoxidized waste cooking oil and its application as a plasticizer for polyvinyl chloride films. *European Polymer Journal*, 99, 142-149.
22. Li, Q., Ma, Y., Song, F., Shu, X., Jia, P., & Zhou, Y. (2020). Synthesis of bio-based plasticizer with improved migration resistance for poly (vinyl chloride). *Green Materials*, 8(4), 203-208.
23. Ma, Y., Song, F., Kong, Q., Li, Q., Jia, P., & Zhou, Y. (2020). Preparation and Performance of Bio-Based Polyol Ester from One-Pot Synthesis of Castor Oil as Nontoxic Poly (Vinyl Chloride) Plasticizer. *Journal of Polymers and the Environment*, 28, 2101-2107.
24. Li, Q., Shu, X., Jia, P., & Zhou, Y. (2020). Preparation of Biomass-Based Ester End-Capped Hyperbranched Poly (ether) s via Facile One-Pot Reaction and Their Performance as Non-Toxic Plasticizers. *Polymers*, 12(4), 913.
25. Feng, Y., Chu, Z., Man, L., Hu, Y., Zhang, C., Yuan, T., & Yang, Z. (2019). Fishbone-like polymer from green cationic polymerization of methyl eleostearate as biobased nontoxic PVC plasticizer. *ACS Sustainable Chemistry & Engineering*, 7(23), 18976-18984.
26. Erythropel, H. C., Börmann, A., Nicell, J. A., Leask, R. L., & Maric, M. (2018). Designing green plasticizers: Linear alkyl diol dibenzoate plasticizers and a thermally reversible

- plasticizer. *Polymers*, 10(6), 646.
27. Huang, Y., Yu, E., Li, Y., & Wei, Z. (2018). Novel branched poly (ϵ -caprolactone) as a nonmigrating plasticizer in flexible PVC: Synthesis and characterization. *Journal of Applied Polymer Science*, 135(32), 46542.
 28. Li, W., Qin, J., Wang, S., Han, D., Xiao, M., & Meng, Y. (2018). Macrodiols derived from CO₂-based polycarbonate as an environmentally friendly and sustainable PVC plasticizer: effect of hydrogen-bond formation. *ACS Sustainable Chemistry & Engineering*, 6(7), 8476-8484.
 29. Zhang, H., Zhu, F., Fu, Q., Zhang, X., & Zhu, X. (2019). Mechanical properties of renewable plasticizer based on ricinoleic acid for PVC. *Polymer Testing*, 76, 199-206.
 30. Jia, P., Xia, H., Tang, K., & Zhou, Y. (2018). Plasticizers derived from biomass resources: A short review. *Polymers*, 10(12), 1303.
 31. Erythropel, H. C., Börmann, A., Nicell, J. A., Leask, R. L., & Maric, M. (2018). Designing green plasticizers: Linear alkyl diol dibenzoate plasticizers and a thermally reversible plasticizer. *Polymers*, 10(6), 646.
 32. Song, F., Jia, P., Xia, H., Zhang, M., Hu, L., & Zhou, Y. (2020). Rosin-derived poly (vinyl chloride) plasticizer: Synthesis, structure, and properties. *Journal of Vinyl and Additive Technology*, 26(2), 180-186.

Figures

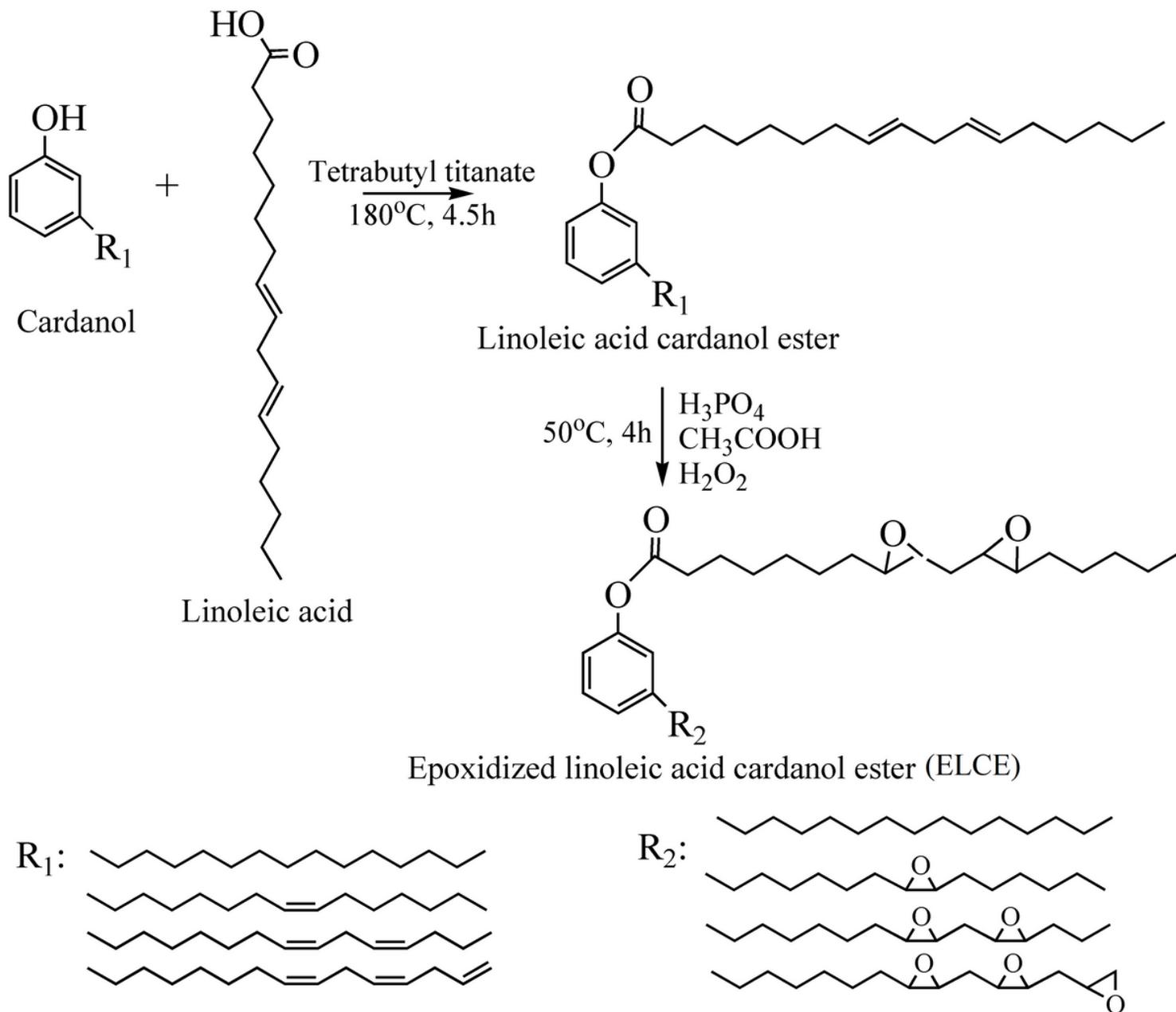


Figure 1

Synthesis of ELCE

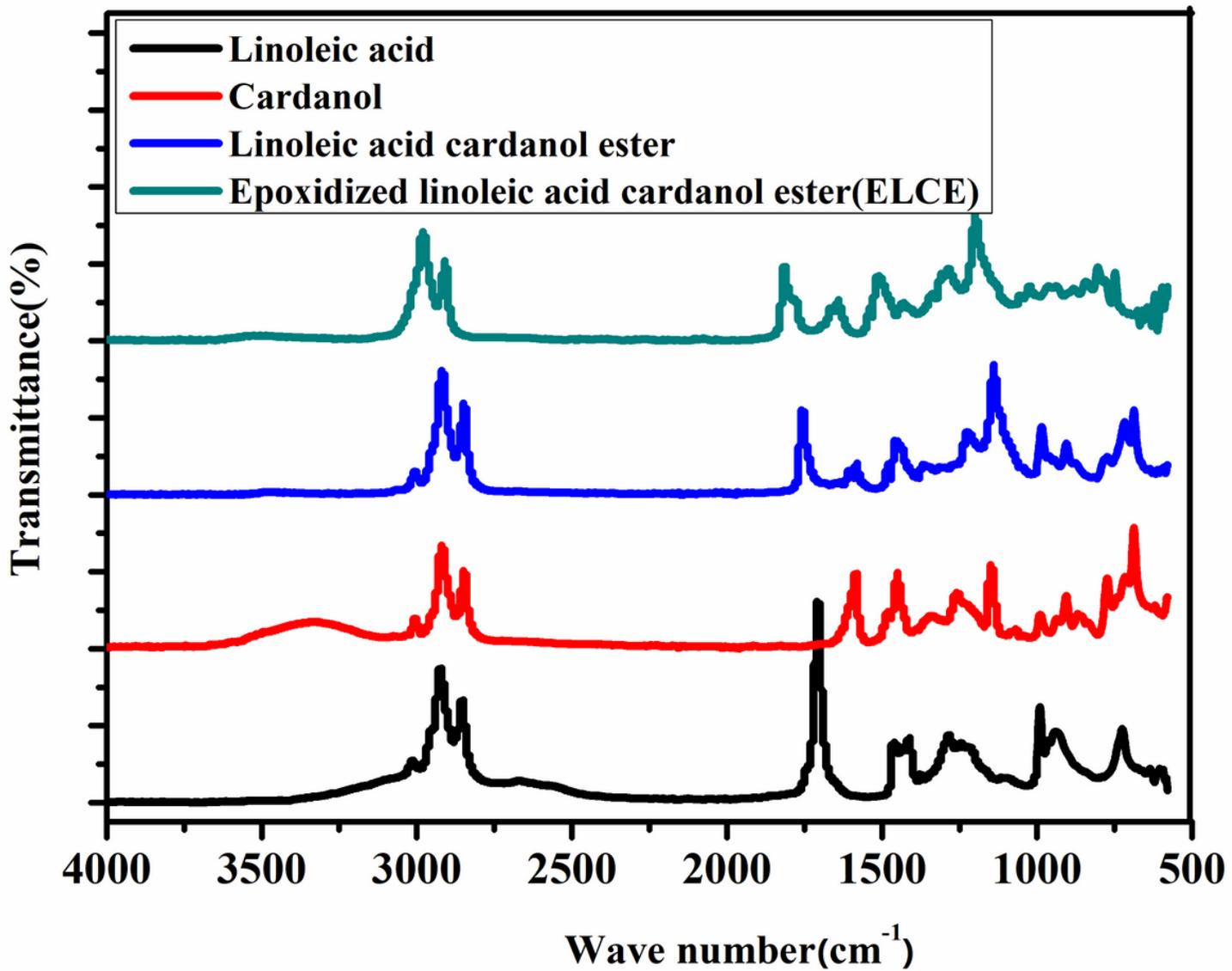


Figure 2

FT-IR of ELCE

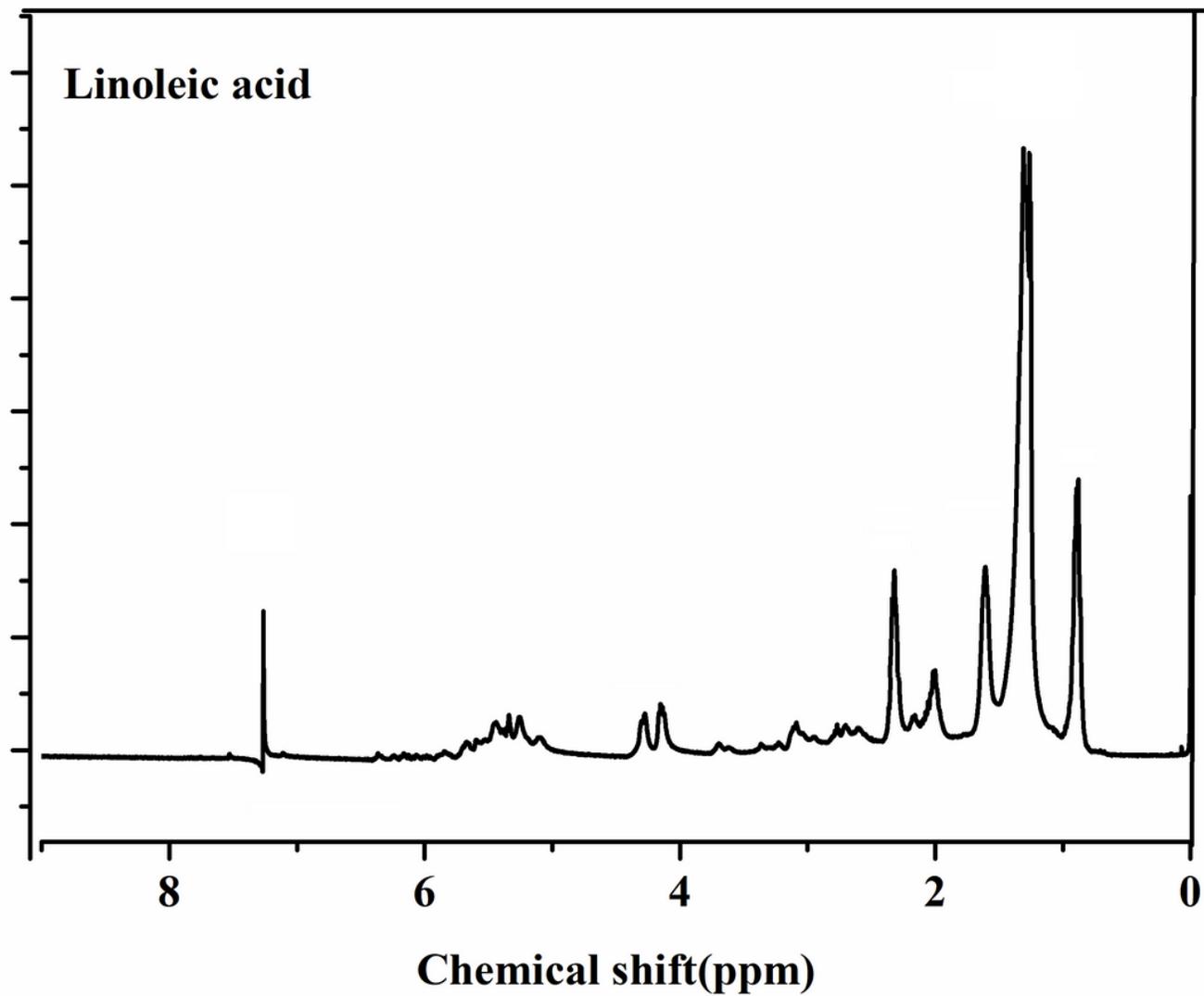


Figure 3

¹H NMR of linoleic acid

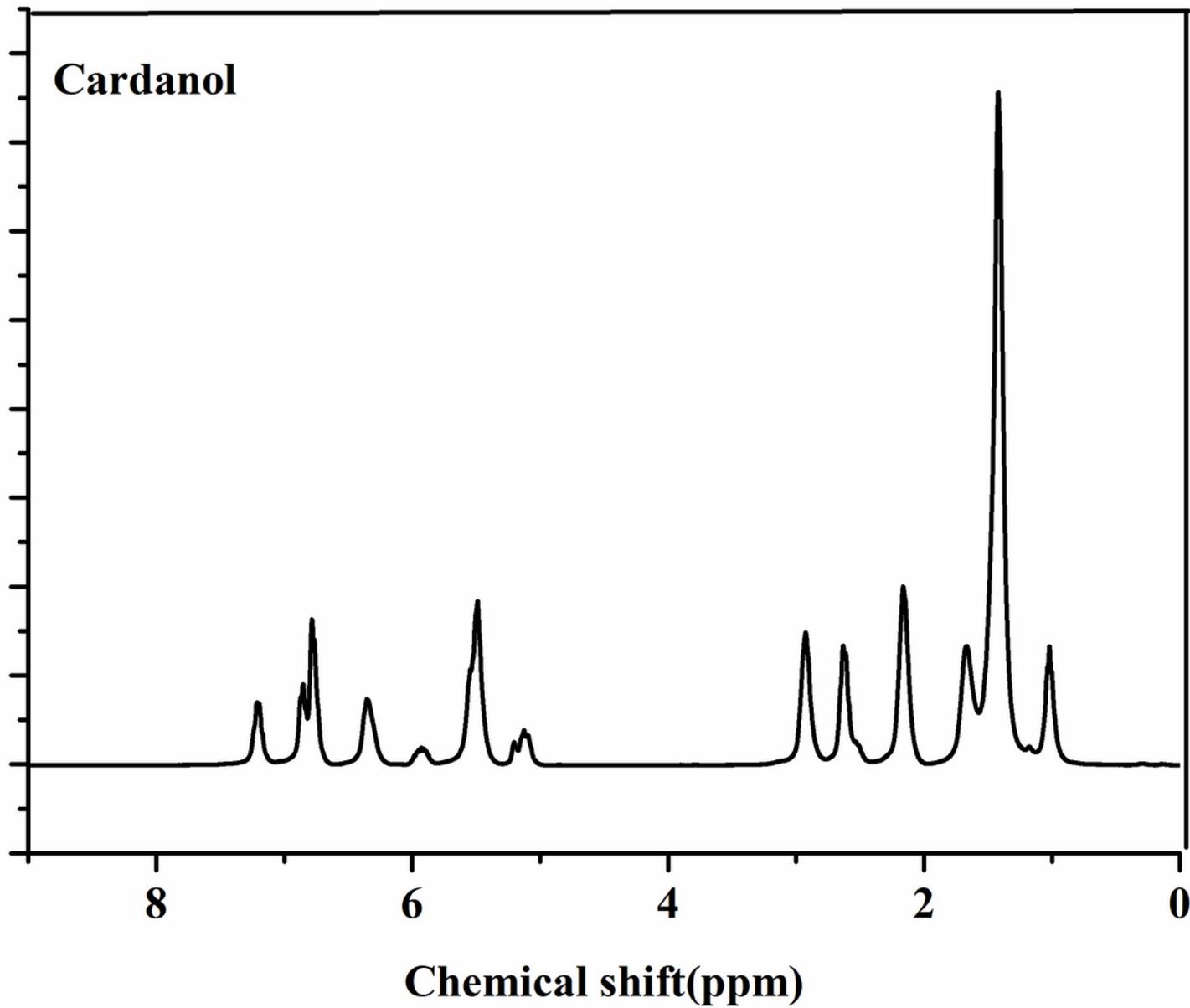


Figure 4

¹H NMR of cardanol

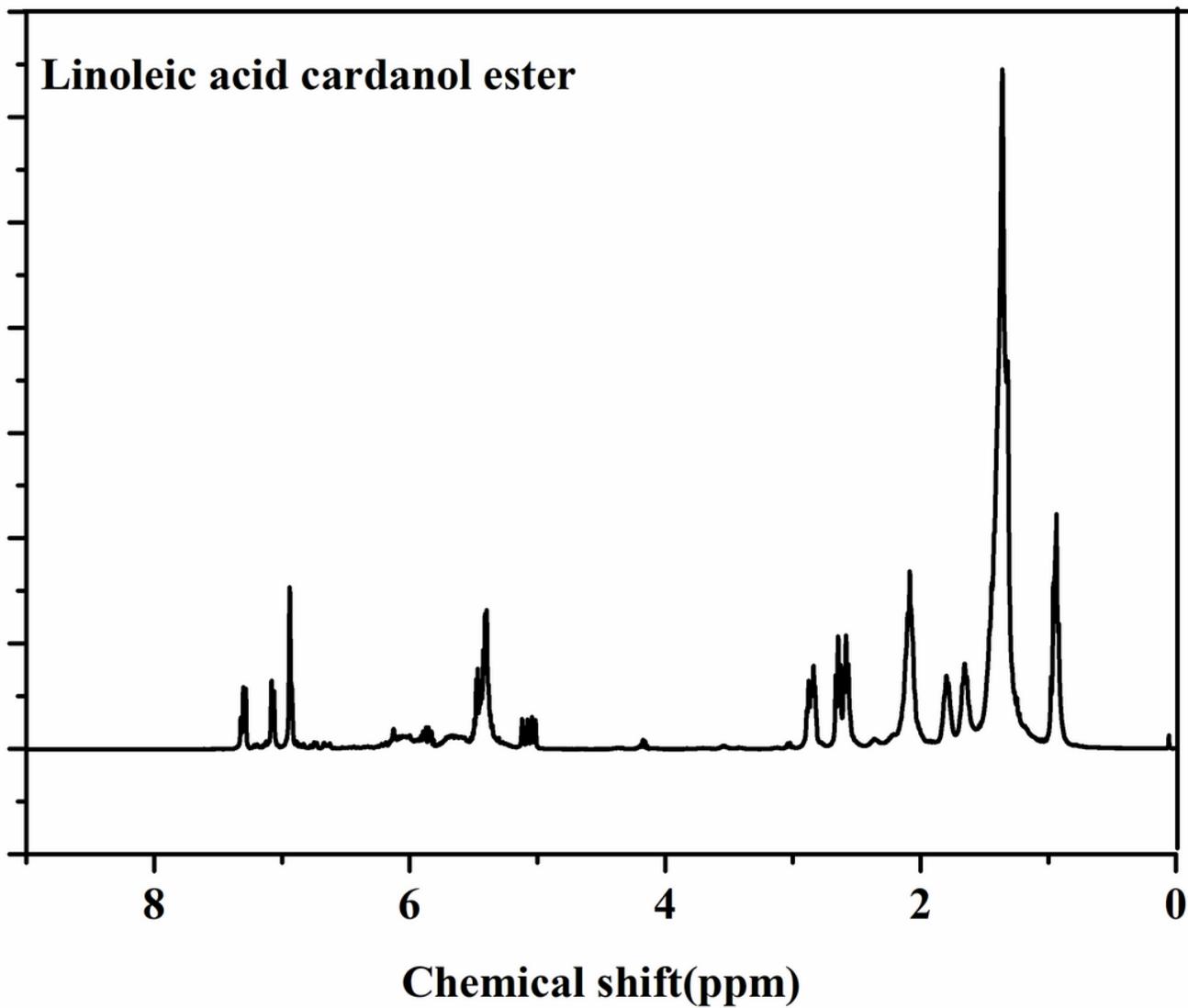


Figure 5

Figure 3 ^1H NMR of linoleic acid cardanol ester

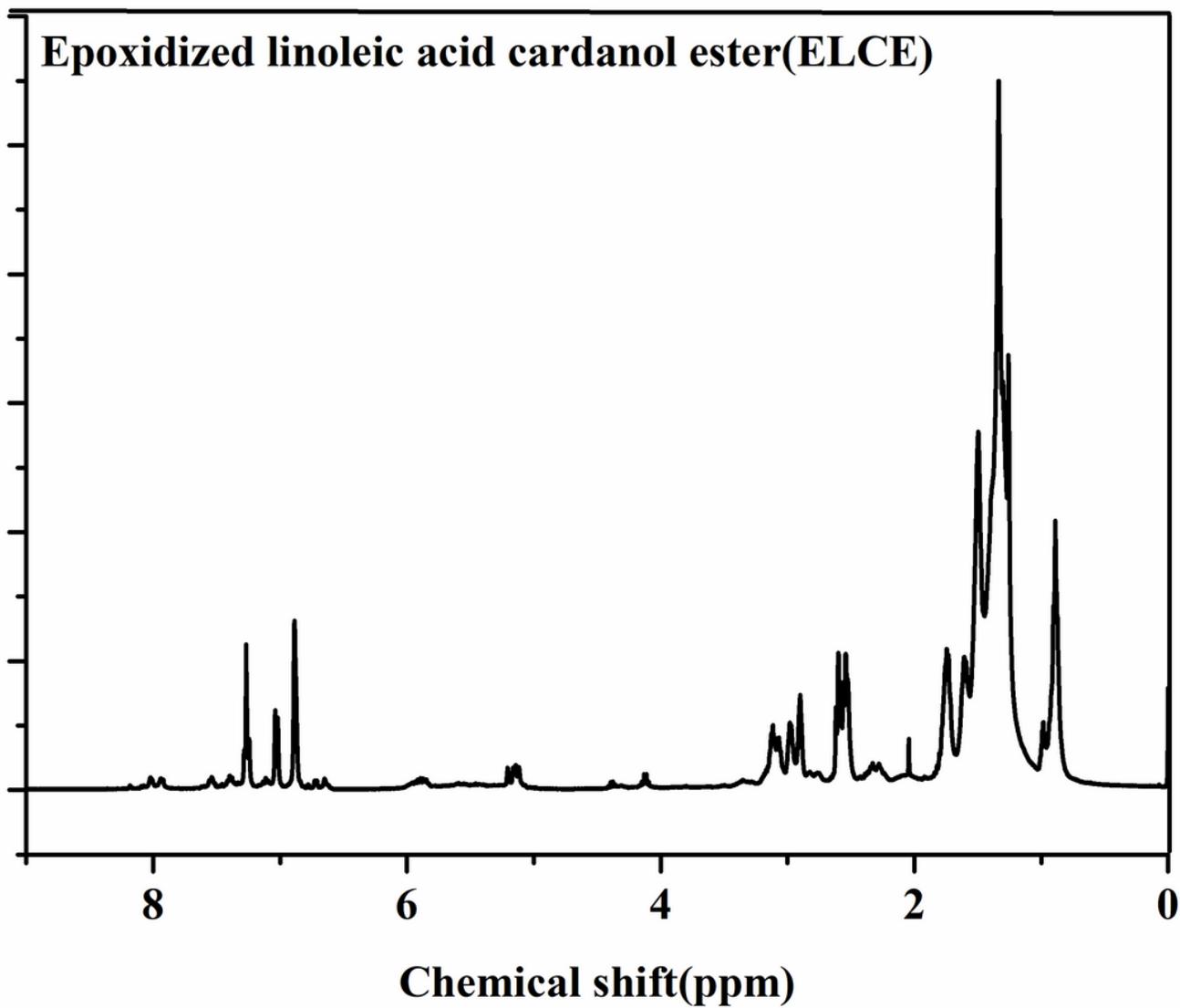


Figure 6

^1H NMR of ELCE

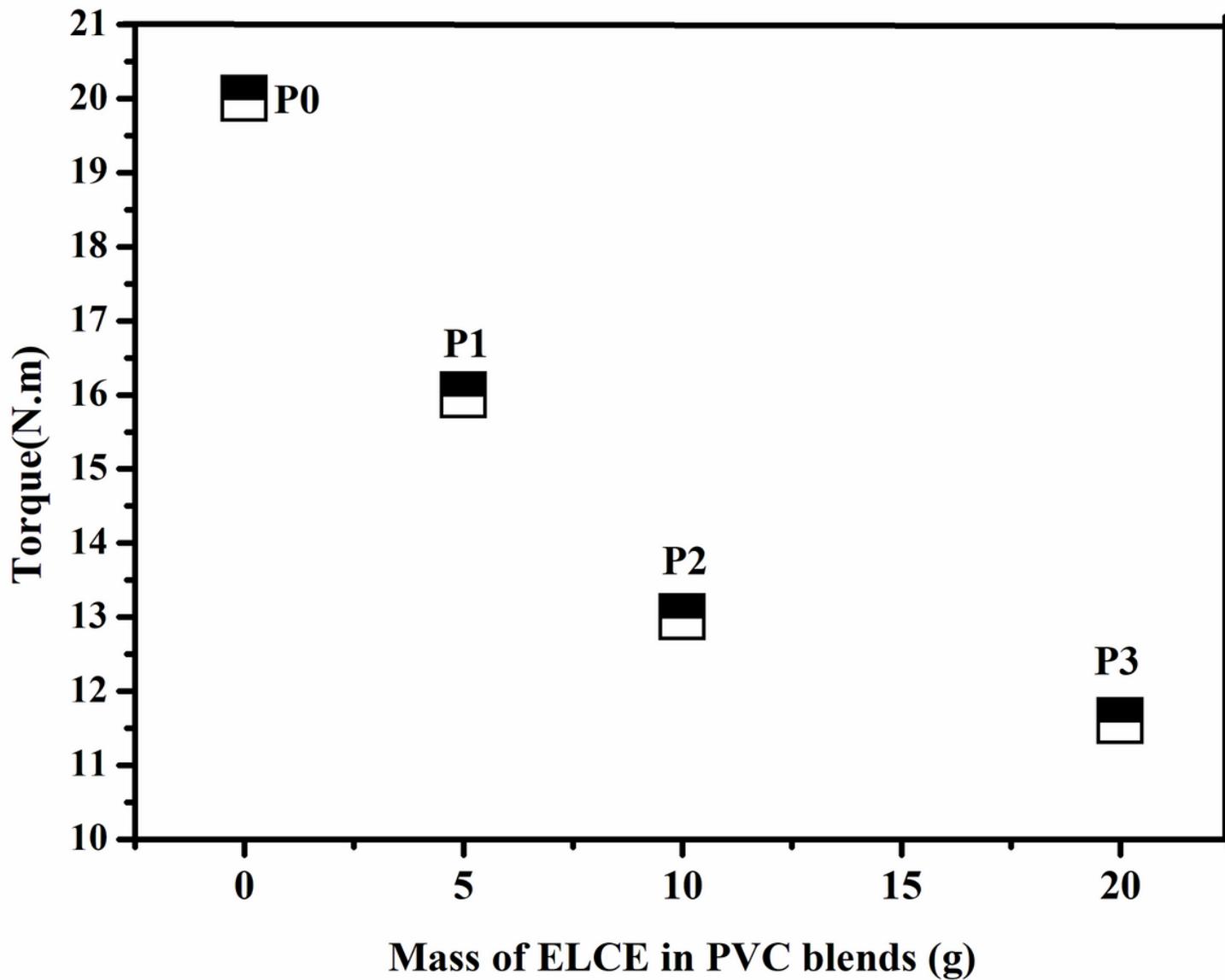


Figure 7

Torque of all plasticized PVC blends

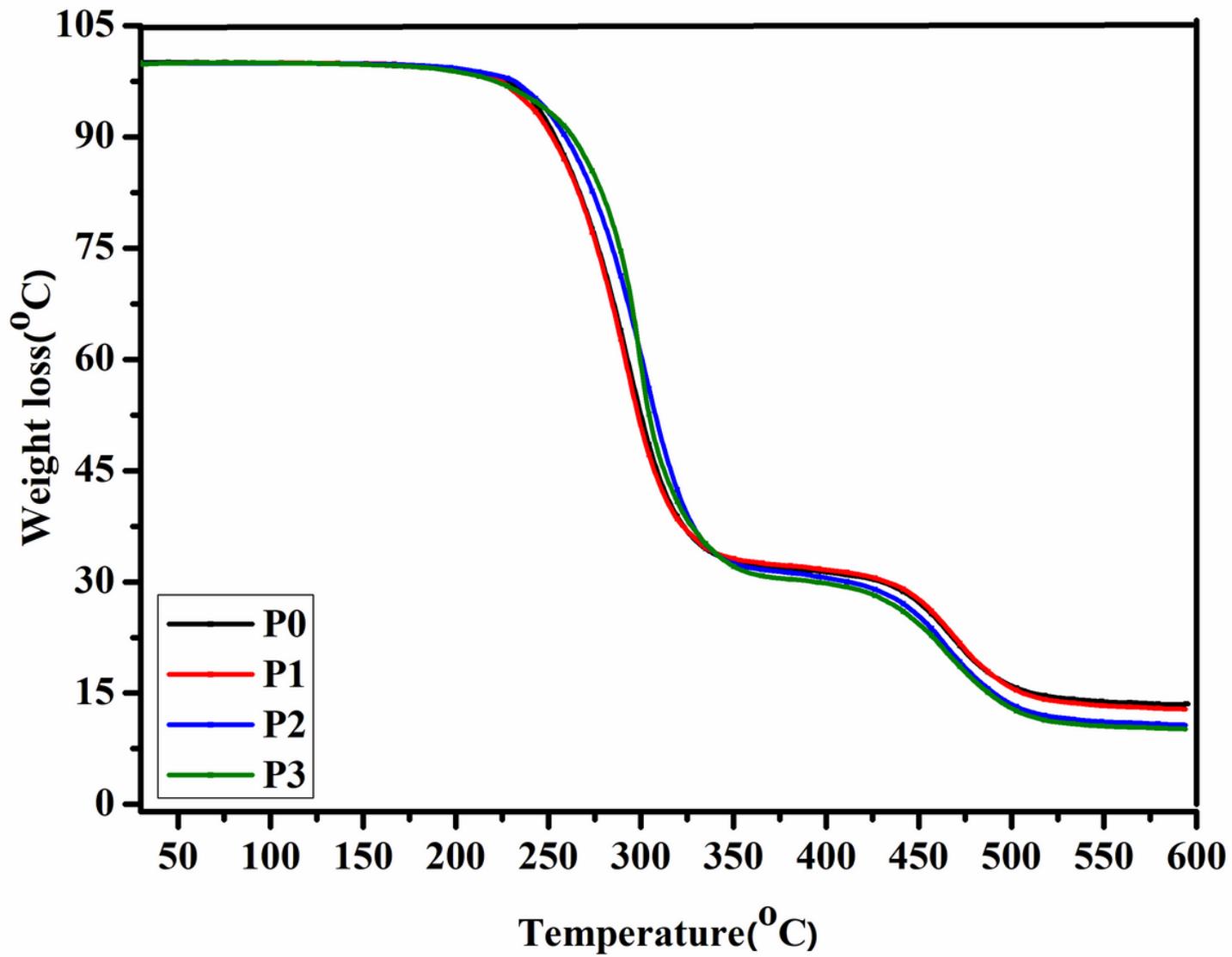


Figure 8

TGA curves of all plasticized PVC blends

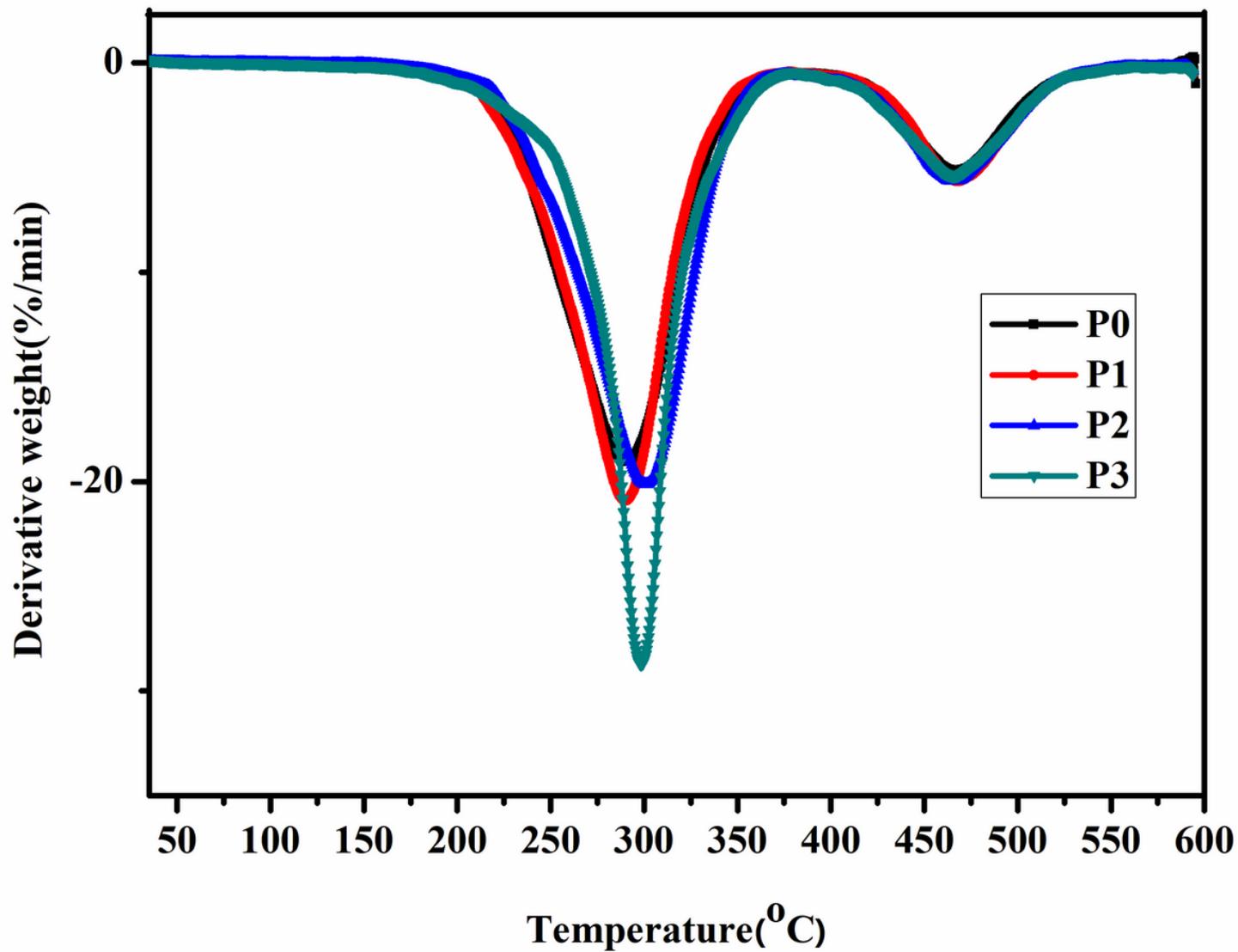


Figure 9

DTG curves of all plasticized PVC blends

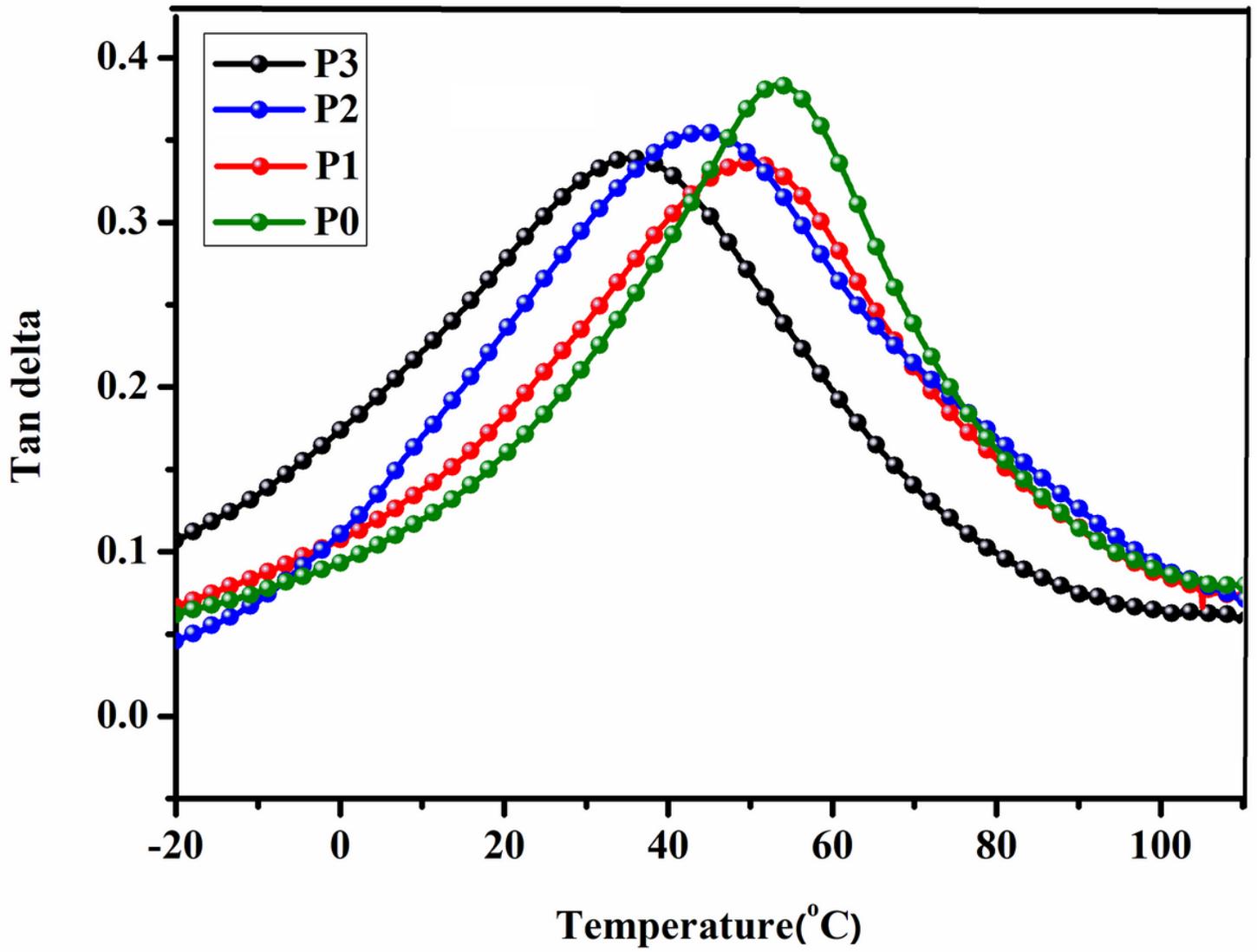


Figure 10

DMA curves of all plasticized PVC blends

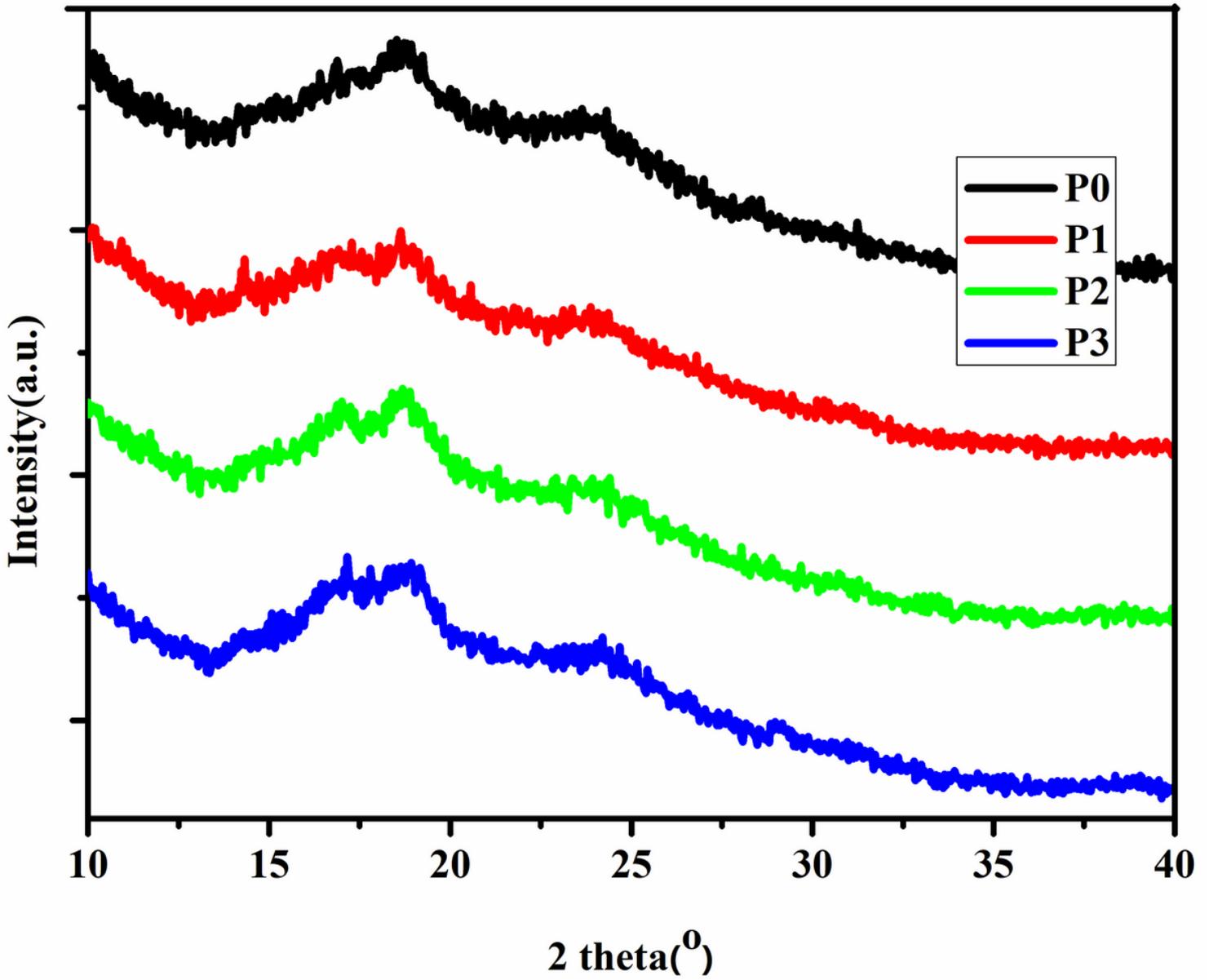


Figure 11

XRD curves of all plasticized PVC blends

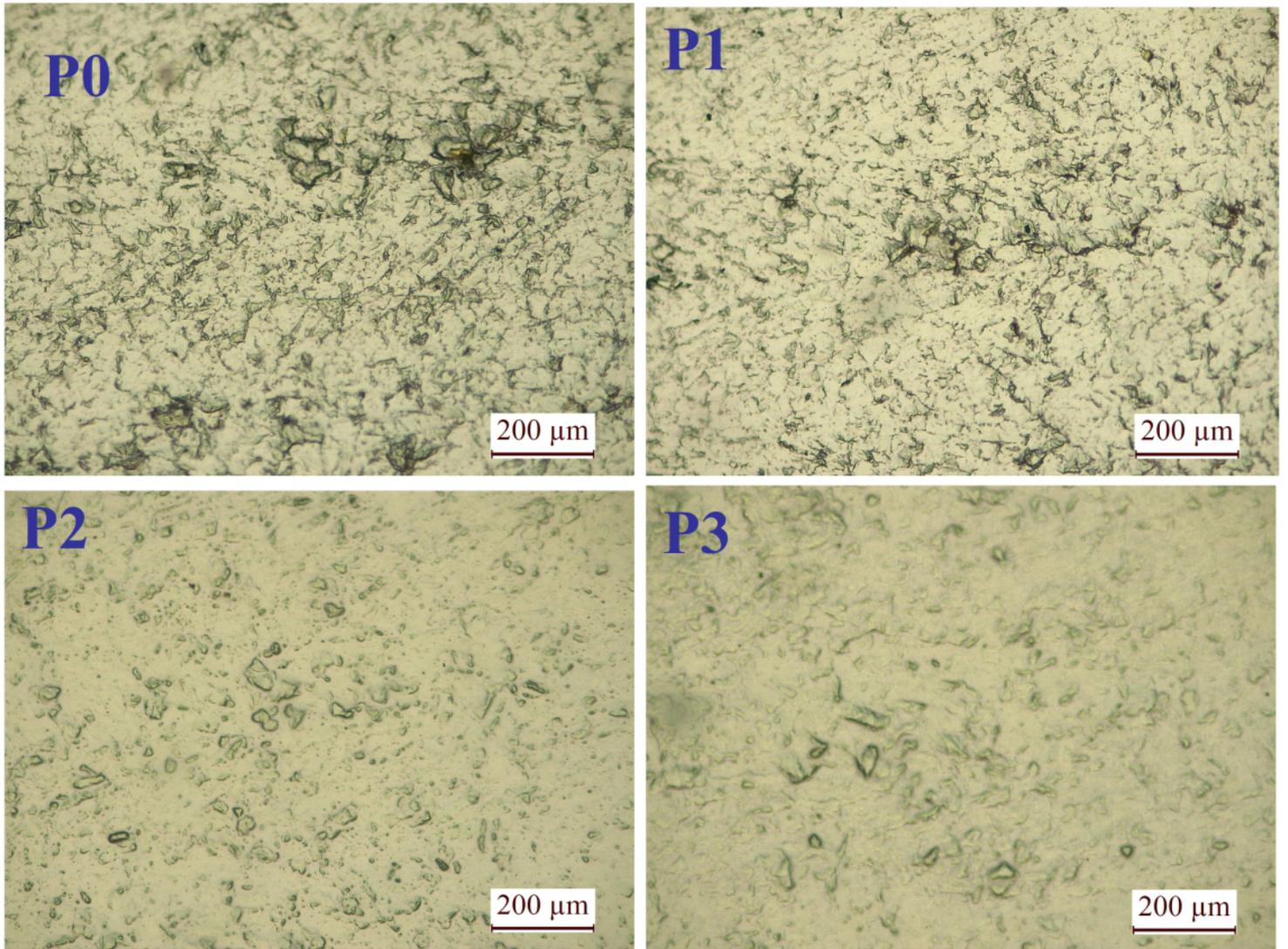


Figure 12

The microstructure of all plasticized PVC blends

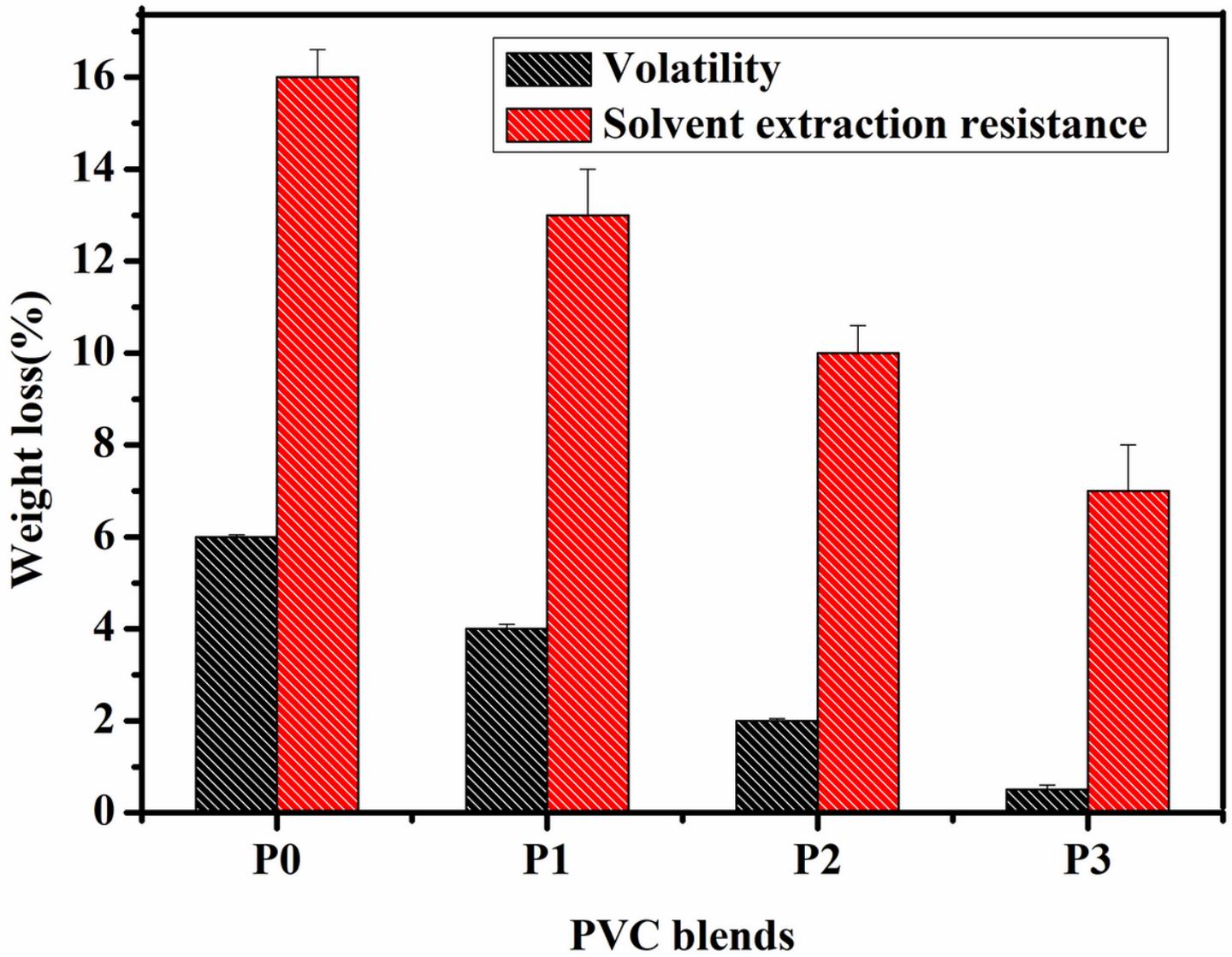


Figure 13

Resistance to volatilization and migration of plasticized PVC blends

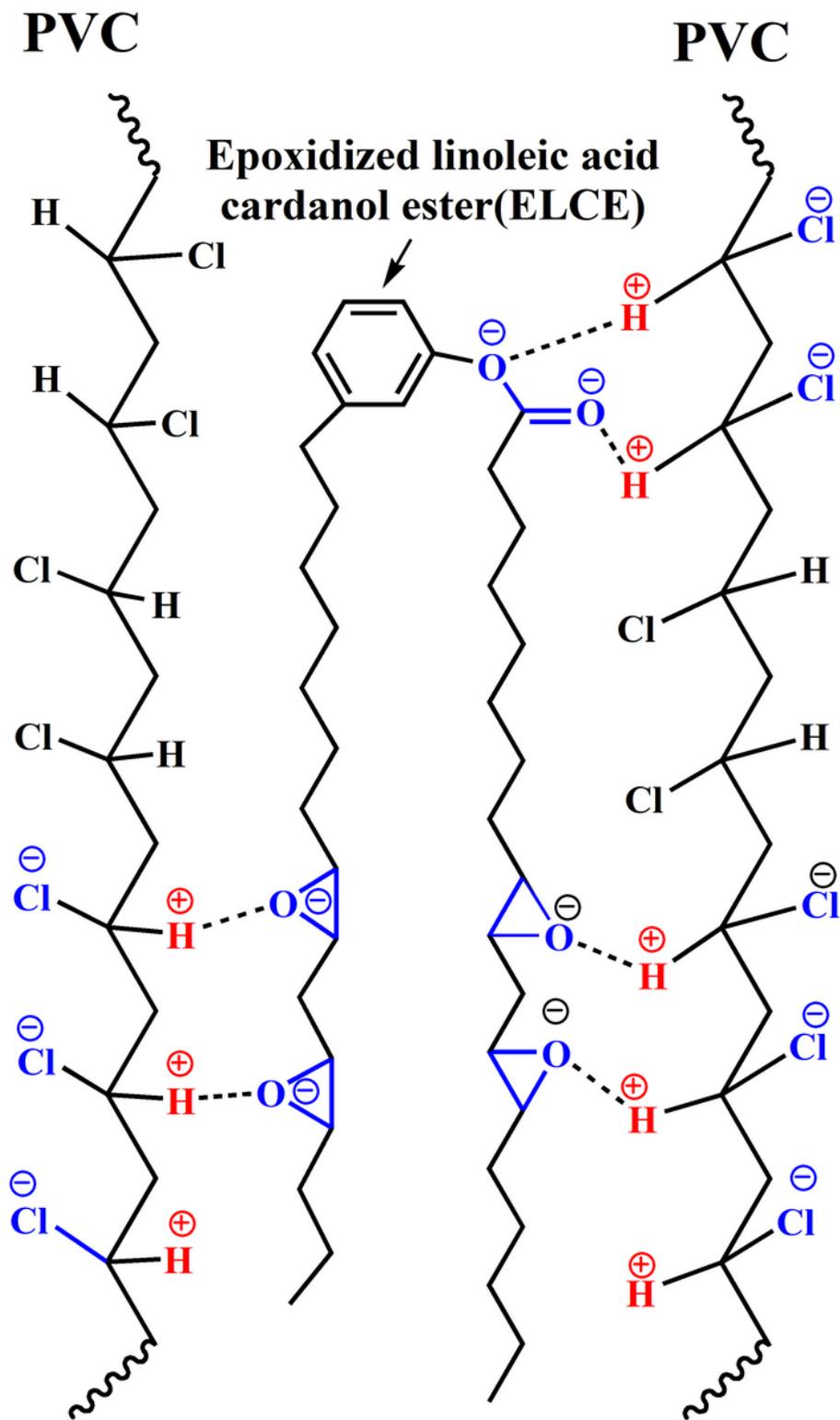


Figure 14

Schematic illustration of the interaction between ELCE and PVC