Supplementary Information

Epoxide Isosorbate Oleic Acid as a Sustainable PVC Plasticizer:

Synthesis, Performance, and Cytocompatibility

Kexin Chang[a], Ruixia Duan [a] *, Suqin He [a,b], Hao Liu[a], Miaoming Huang[a], Wanlin Xu[a], Chengshen Zhu[a],

Zhe Chu [c]*, Tao Li [d], Wentao Liu [a]

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a. *School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, China.*

b. *Henan Key Laboratory of Advanced Nylon Materials and Application, Zhengzhou University, Zhengzhou, 450001, China.*

c. *The intersection of Gongye Road & Jianshe Road, Zhengzhou, 450000 China*

d. *School of Physics and Electronic Engineering, Henan Key Laboratory of Magnetoelectronic Information Functional Materials, Zhengzhou University of Light Industry, Zhengzhou 450002, China*

*Corresponding authors: duanrx@zzu.edu.cn (Ruixia Duan); chu@ztcc.com (Zhe Chu)

S1 Supplementary Details of the Experimental Section

The purification process of the product

The product, isosorbide oleate (IOA), was treated with a 0.25 mol/L NaOH solution to remove residual oleic acid from the reactants. After centrifugation, the upper layer was collected and washed with deionized water, then water in the organic phase was removed by rotary evaporation to obtain the brown product-isosorbide oleate (IOA). After the epoxidation reaction was complete, the catalyst was removed by centrifugation, and the product was washed with deionized water until neutral. Finally, residual water was removed by rotary evaporation to obtain the yellow epoxy isosorbide oleate product.

The determination of the epoxy value of the plasticizer

The determination of the epoxy value of the plasticizer is carried out in accordance with GB/T 1677-2008 "Determination of Epoxy Value of Plasticizers," with the mean of three measurements taken as the result. The detailed experimental procedure is as follows. Weigh 0.5–1 g of the sample and place it in a 250 mL conical flask. Accurately add 20 mL of hydrochloric acid–acetone solution, seal the flask, shake thoroughly, and let stand in a dark place for 30 minutes. Then add 5 drops of the mixed indicator and titrate with 0.15 mol/L sodium hydroxide standard solution until a blue-violet color is reached, performing a blank experiment simultaneously.

The epoxy value is expressed as mass fraction X and is calculated according to the formula 1:

$$X = \frac{\left[V - \left(V_1 - \frac{V_2}{G} \times W\right)\right] N \times 0.016}{W} \times 100 \ \% \tag{1}$$

Where, V is the volume of standard sodium hydroxide titrant consumed in the blank test, mL; V_1 is the volume of standard sodium hydroxide titrant consumed in the sample test, mL; V_2 is the volume of standard sodium hydroxide titrant consumed for determining the acid value in the sample, mL; N is the concentration of the standard sodium hydroxide titrant, mol/L; W is the mass of the sample, g; G is the mass of the sample used for acid value determination, g; and 0.016 is the molar mass of oxygen, in g/mol.

PVC Specimen Preparation

10 g of PVC were placed in a 250 mL beaker with 150 mL of tetrahydrofuran. The beaker was sealed with a film and placed on a strong magnetic stirrer. After approximately 4 hours of stirring, a clear solution was obtained. A predetermined amount of plasticizer was then added, and stirring continued for another 4 hours to obtain a homogeneous solution. The solution was poured into a Petri dish with a diameter of 15 cm and left in a fume hood until the solvent fully evaporated, resulting in PVC specimens. The plasticizer content is expressed as a mass fraction. For example, a specimen containing 12 g of PVC and 6 g of EIOA is designated as EIOA-50.

In vitro cytotoxicity test

The in vitro cytotoxicity test used L929 mouse fibroblast cells, with modified Eagle's medium (DMEM) as the culture medium. The quantitative MTT assay was employed for **direct contact experiments.** The experimental group had EIOA concentrations of 0.01 mg/mL, 0.05 mg/mL, and 0.1 mg/mL; and **the positive control group** contained dimethyl sulfoxide (DMSO) at concentrations of 0.01 mg/mL, 0.05 mg/mL, and 0.1 mg/mL; t**he blank group contained only complete culture medium without EIOA or DMSO**, with all other test conditions identical. The test duration was 24 hours, with five replicates per group, and the average value was taken as the final result. Repeat the experiment three times and report the results of a representative dataset for each plasticizer. Apply the Mann-Whitney nonparametric test to assess differences in survival rates between the control and experimental conditions, considering a p-value less than 0.05 as statistically significant.

DMA characterization

The dynamic thermomechanical behavior of the specimens was analyzed with a Q800 dynamic mechanical analyzer from TA Instruments, USA, at a frequency of 1 Hz, a heating rate of 3 °C/min, and over a temperature range of -60 to 100 °C.

Mechanical characterization

The prepared PVC film is cut into dumbbell-shaped specimens (gauge length 13 mm, width 2 mm, and thickness 0.5 ± 0.03 mm) using a standard cutter. The tensile properties are tested at room temperature (25 ± 5°C) with a controlled stretching rate of 100 mm/min. Each sample is tested 5 times under the same conditions, and the average value is taken as the final tensile property result.

Characterization of surface and transparency

The cross-sectional morphology of the SEM specimens was examined using a FEI benchtop scanning electron microscope. The cross-sections were prepared in liquid nitrogen and observed after gold sputtering.

The transmittance spectra of PVC samples were measured using the UV-9000S ultraviolet spectrophotometer from Shanghai Yuanxi Instruments Co., Ltd., China. The prepared polyvinyl chloride films were cut into rectangles measuring 20 mm × 40 mm and placed on the film sample holder for measurement, with a wavelength range of 200–900 nm, using air as the blank reference.

Contact angle measurements were conducted using the HARKE-SPCAX2 optical contact angle goniometer to analyze the water contact angle. Test specimens were cut into approximately 10 mm × 10 mm, and a 0.4 μL water droplet was applied to the sample surface for testing. The left and right contact angles were measured from optical images of the droplets, and the average of 3 sets of angles for the same sample was used as the final data.

The weight loss (WL) was calculated according to equation 2.

$$WL = \left(\frac{W_1 - W_2}{W_1} \right) \times 100 \qquad (2)$$

where W_1 was the initial weight of PVC specimens and W_2 was the final weight of the test PVC specimens. The weight loss data were collected using the average value of five test samples.

Table S1. TGA data of PVC samples

Sample	PVC	DOTP-50	EIOA-40	EIOA-50	EIOA-60
$T_{5\%}$ (°C)	193.3 ± 2.1	285.1 ± 3.0	293.1 ± 3.3	298.9 ± 3.5	301.6 ± 5.4
$T_{10\%}$ (°C)	258.0 ± 2.5	296.6 ± 3.3	301.1 ± 3.7	308.4 ± 4.4	310.1 ± 6.3
$T_{50\%}$ (°C)	308.6 ± 2.2	327.6 ± 5.3	375.0 ± 4.1	378.1 ± 3.2	388.6 ± 6.1

Table S2. Mechanical properties data of PVC specimens

Sample	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Shore hardness (HA)
PVC	35.9 ± 1.3	444.5 ± 13.5	549.1 ± 2.8	98.2 ± 0.5
DOTP-50	28.9 ± 1.1	607.9 ± 19.0	9.2 ± 0.5	88.3 ± 0.8
EIOA-40	26.6 ± 0.3	599.5 ± 6.8	6.9 ± 0.1	92.5 ± 0.4
EIOA-50	25.4 ± 0.2	636.5 ± 13.6	6.2 ± 0.1	88.3 ± 0.5
EIOA-60	22.7 ± 0.2	656.3 ± 8.4	5.5 ± 0.2	84.4 ± 0.8

Table S3. Positron annihilation lifetime parameters of samples

Free Volume	R (Å)	V (Å³)	Free Volume Ratio (%)
PVC	2.82	94.46	1.09
EIOA-50	2.97	109.63	1.59
DOTP-50	2.95	107.68	1.61

Table S4 Performance Comparison of EIOA with Commercial Plasticizers from Literature Data

Plasticizer(phr)	DOTP(50)	DEHP(40)	DINCH(40)	ATBC(50)	EIOA(50)
Chemical Type	Petrochemical	Petrochemical	Petrochemical	Bio-based	Bio-based
Bio-based Content / %	0%	0%	0	~100%	~100%
Tg of Plasticized PVC / °C	~21	~23.2	~25	~27	23.3
Tensile strength (MPa)	~28.9	11.8	8.8	12.9	25.4
Elongation at break / %	~607.9	96	87	314.7	636.5
T5% / °C	~285.1° C	~230	260	220	298.9
Weight Loss in n-hexane 25 °C，for 24h / %	~24	30	15	10	1.8
Cytotoxicity	Low	Toxic	Low	Non-toxic	Non-toxic
Ref	This work	Ref[19, 20]	Ref[20]	Ref[5]	This work

Here we systematically reviewed high-quality journal literature and compiled the key performance data of EIOA, comparing it with several important commercial plasticizers you mentioned, including the conventional phthalate Di(2-ethylhexyl) phthalate (DEHP), the novel petroleum-based Di-isononyl-cyclohexane-1,2-dicarboxylate (DINCH), and the bio-based acetyl tributyl citrate (ATBC).

This comparative table encompasses several characteristics for evaluating the merits of plasticizers, including plasticization efficiency, mechanical properties, migration resistance, mobility barrier, and thermal stability, along with two key attributes: bio-based content and cytotoxicity. Through this comprehensive literature comparison, it is evident that PVC plasticized with EIOA performs excellently, with plasticization efficiency comparable to DEHP/DOTP, migration resistance significantly superior to DOTP and ATBC, and the unique advantages of being 100% bio-based and non-cytotoxic. This makes EIOA not only a viable alternative but also a highly competitive candidate in the pursuit of both high performance and sustainability.

S2 Preliminary Environmental Benefit Assessment

(1) Definition of Goal and Scope

This is the most critical step, as it determines the boundaries of the calculation. We clearly defined the goal and boundary as 'production of 1 kg of EIOA from cradle to gate.' For the time being, we are excluding product transportation, use phase, and disposal stage. These stages have relatively little impact on the plasticizer itself and the data is difficult to obtain.

(2) Process Flow Diagram and Data Collection

FigureS1 presents a simple process flow diagram of EIOA, and the data for each step within the system boundary is determined as follows.

Raw material. Since isosorbide and oleic acid are derived from biomass sources such as corn or waste oils, we adopt a key assumption that biogenic carbon is carbon-neutral. That is, the CO_2 absorbed during plant growth offsets the CO_2 released upon eventual decomposition. Therefore, we assume that the carbon footprint of these two materials is zero. Chemicals such as catalysts and solvents: Because the amount of catalyst used is small and solvents can be recycled, their contributions are neglected in the estimation.

Energy Consumption. Energy consumption is primarily in the form of electricity. Estimate the total electricity usage (kilowatt-hours, kWh) for synthesizing 1 kilogram of EIOA in the laboratory, including processes such as stirring, heating, and cooling. A rough estimate can be calculated based on the power (kW) of the heating mantles and magnetic stirrers used and the operating time (h): Power (kW) × Time (h) = Electricity consumption (kWh). If the reaction heating is supplied by natural gas or steam, its consumption should also be estimated. For simplification, all calculations here are based solely on electricity.
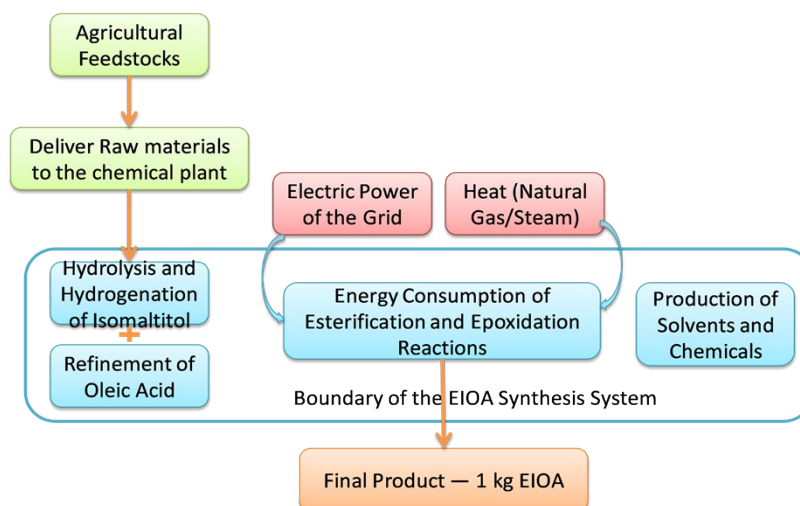

Figure S1　EIOA Production Process Flow and Carbon Emission Boundaries

(3) Calculating Carbon Footprint

Use the formula: Carbon Footprint = Σ (Activity Data × Emission Factor) For grid electricity, the emission factor is taken as the Chinese national average, approximately 0.6 kg CO_2e/kWh (Source: Ministry of Ecology and Environment of China, 2024 database). Table S5 shows the preliminary estimation of carbon footprints of two plasticizers.

Project	EIOA	DOTP	Data Sources and Notes
Carbon Footprint of Raw Materials (kg CO₂e)	0	2.5	The raw materials of EIOA are all bio-based and assumed to be carbon neutral; DOTP is produced from P-Xylene, with a typical range of 2.5-3.2 kg CO₂e / kg（Ecoinvent Database）。
Energy Consumption in the Production Process (kWh)	8	6	The laboratory-scale preparation of EIOA requires two reactions, esterification and epoxidation, which result in relatively high energy consumption; in contrast, DOTP involves only a single esterification reaction, and its process is mature, leading to higher energy efficiency.
Energy and Carbon Footprint(kg CO₂e)	4.8	3.6	calculated by Formula: Carbon Footprint = Σ (Activity Data × Emission Factor)
Total Carbon Footprint (kg CO₂e)	4.8	6.1	Sum Calculation

*Note: To ensure a fair comparison, the electricity emission factor is based on the average emission factor of the Chinese power grid, 0.6 kg CO₂e/kWh (Source: Ministry of Ecology and Environment of China, 2024 database).

（4）Analysis of Comparative Results

Although the energy consumption of the EIOA synthesis process may be slightly higher, its 100% bio-based feedstock reduces the overall carbon footprint by approximately 25% compared to petroleum-based DOTP.

S3 Hardness of PVC Specimens after Migration

The hardness and transparency of all specimens changed to varying degrees after migration, therefore tests on the hardness and transparency of all specimens were conducted. Figure S2 presented the Shore hardness of various PVC specimens after being immersed in different reagents for 10 d. All specimens demonstrated a low mass loss rate in distilled water, with minimal changes in hardness and transparency. In the other five environments, the hardness of all specimens increased, as the incorporation of plasticizers enhanced the flexibility of PVC, while migration resulted in an increase the hardness of specimens. Notably, after 10 d in the presence of activated carbon, petroleum ether, and n-hexane, the hardness of DOTP-50 exhibited a greater increase than that of the EIOA series specimens.
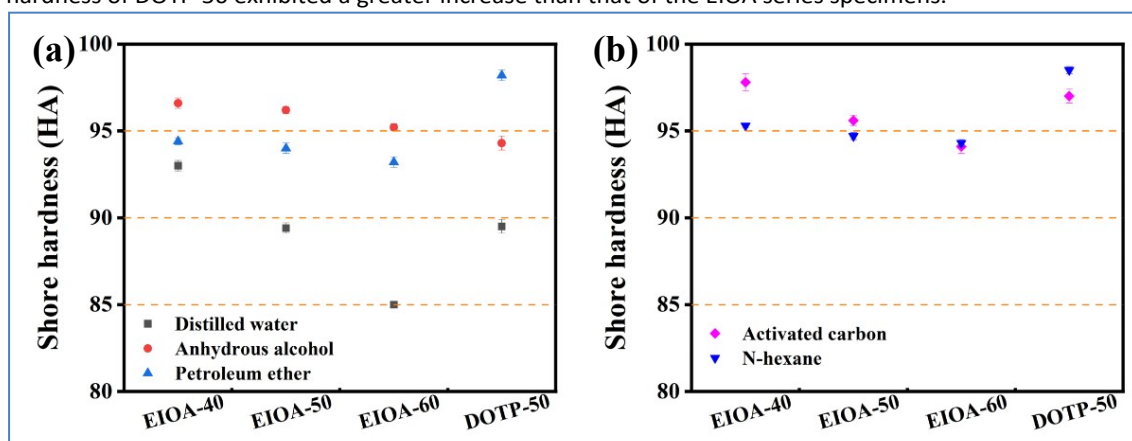

Figure S2. Shore hardness of PVC specimens after migration immersed in (a) distilled water, anhydrous ethanol and petroleum ether; (b) activated carbon and n-hexane

Figure S3 shows the surface microscope images of different PVC specimens after being immersed in various solvents. The surfaces of all PVC specimens were flat and smooth prior to testing, and EIOA-50 exhibited fewer surface defects compared to DOTP-50. Following the migration resistance test, all samples showed varying degrees of damage, among them EIOA-60 exhibiting the most severe surface damage.

After soaking in water for 10 d, the surfaces of all specimens remained relatively flat and smooth. After soaking in absolute ethanol for 10 d, the surface morphology of DOTP-50 showed numerous gaps, and a small amount of damage was also observed on the surface of the EIOA specimen. After soaking in petroleum ether for 10 d, the DOTP-50 surface exhibited many cross cracks accompanied by defects, while the EIOA specimen's surface was partially damaged but still relatively flat and smooth. After soaking in n-hexane for 10 d, the DOTP-50 surface displayed a greater number of linear cracks along with defects, which was associated with the higher mobility and faster migration rate of DOTP, whereas only minor damage was noted on the surface of the EIOA specimen. The surface conditions of different specimens reflect varying migration scenarios, and DOTP-50 showed the most significant damage in the same batch of tests, closely related to the migration rate of DOTP-50.
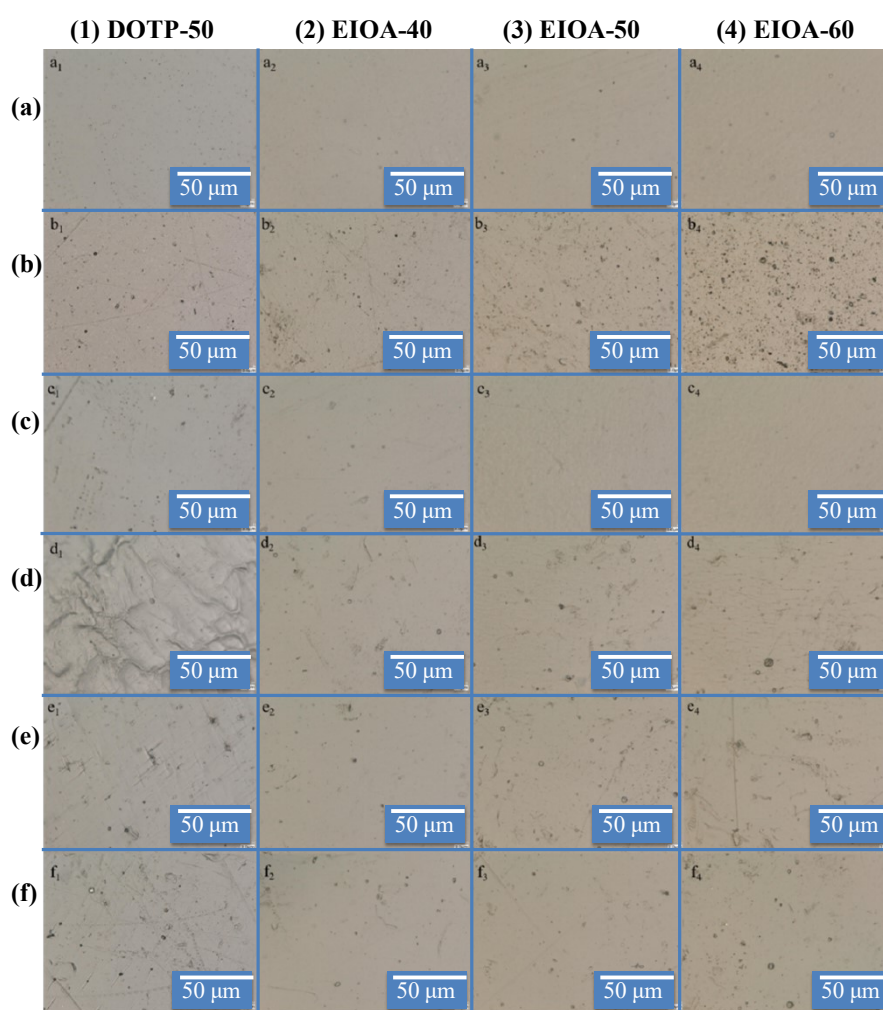

Figure S3 Microscopic images of PVC specimens (the scale is 50 μm): the vertical direction are the microscope photos before soaking (a) and after 10 days in activated carbon (b), distilled water (c), anhydrous ethanol (d), petroleum ether (e), n-hexane (f); and the horizontal direction are DOTP-50 (1), EIOA-40 (2), EIOA-50 (3), EIOA-60 (4), respectively.

S4 Transparency of PVC Specimens after Migration

The UV-VIS spectra of different PVC pieces are shown in Figure S4(a). With the increase of EIOA content, the UV transmittance of the plasticized PVC specimen decreased, indicating that it had a certain resistance to UV light. In the visible light region, the transmittance of PVC test film was only 60%, and the transmittance of DOTP-50 was 85.5%. The EIOA-50 piece had the best transparency of 87%. The transparency of pure PVC flake was improved after the addition of plasticizer, which was suitable for application in the field of transparent film. Because the plasticizer could enter the crystallization zone of PVC so as to reduce its crystallinity. At the same time, the plasticizer could provide a certain free volume which can improve the transparency and flexibility of PVC piece to a certain extent.

Figure S4(b)-(f) presents the transparency of different PVC specimens after soaking in solvents for 10 days. Figure S4 (b) showed that the transparency of all samples remained mostly unchanged after soaking in distilled water for 10 days. Figure S3 (c) showed that the transmittance of DOTP-50 decreased to about 50% after immersion in anhydrous ethanol for 10 days, while the EIOA sample maintained a nearly unchanged transparency. Figure S3 (d) indicated that, after soaking in petroleum ether for 10 days, all samples experienced a slight decrease in transparency, but remained largely stable. Figure S3 (e) presented the results performed on activated carbon for 10 days, where the transmittance of EIOA-50 and DOTP-50 was around 80%. The transparency of EIOA-60 decreased with increasing plasticizer content, dropping to 60%, likely due to a lower Young's modulus and hardness. Figure S3 (f) showed that after soaking in n-hexane for 10 days, all EIOA samples maintained a transparency of over 80%, with DOTP-50 achieving a transmittance of 78%. In conclusion, EIOA-50 samples retained higher transparency than DOTP-50 after various migration tests, which is closely related to its lower migration rate.
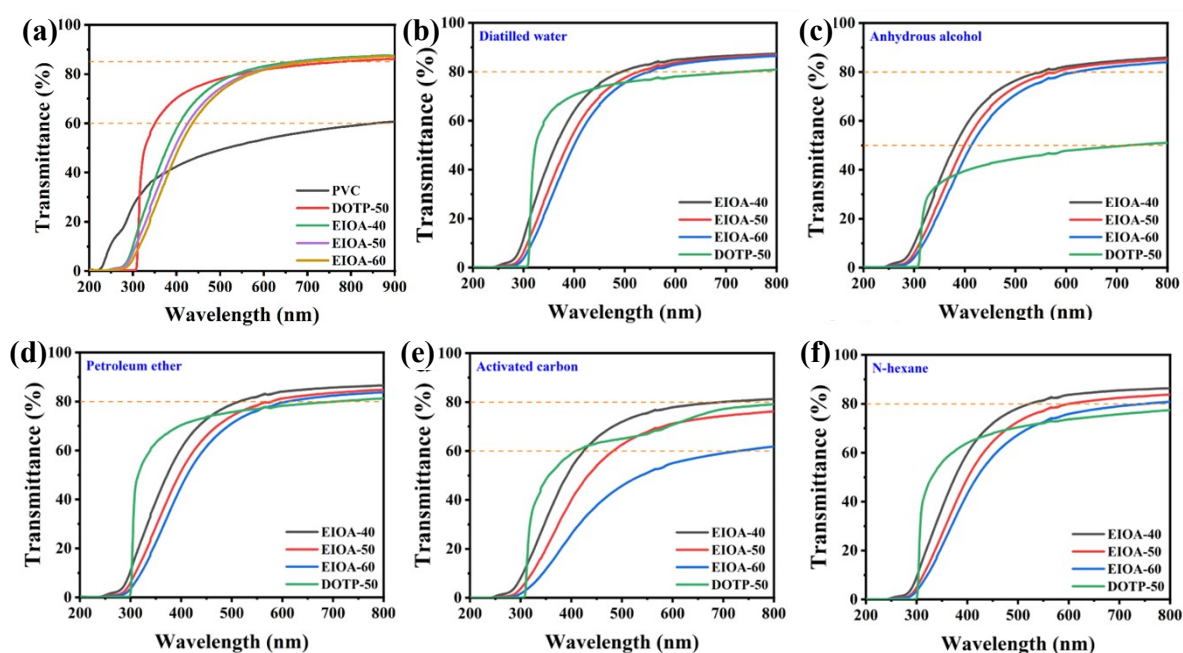

Figure S4. UV-vis spectrum of PVC specimens before emigration (a) and after emigration in distilled water (b), anhydrous ethanol (c), petroleum ether (d), activated carbon (e) and n-hexane (f) for 10 d