

Supplementary Information

Closed-loop utilization of polyester in the textile industry

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1. General

1.1 Reagents

Ethylene glycol (EG, analytically pure, $\geq 99.5\%$) was purchased from Shanghai Titan Technology Co., Ltd. Commercial BHET was purchased from Shanghai Adamas Reagent Co., Ltd. Polyester ($M_n \approx 1.6 \times 10^4$ g/mol) fiber was self-made in the laboratory. Anhydrous potassium carbonate (analytically pure) was purchased from Sinopharm Chemical Reagent Co., Ltd. Nuclear magnetic deuterium reagent deuteromethanol (97%, including TMS) was purchased from Shanghai Haohong Biomedical Technology Co., Ltd. Ethylene glycol antimony (antimony content is about 200 ppm) as polycondensation catalyst was purchased from Shanghai McLean Biochemical Technology Co., Ltd. The waste clothes were donated by the Love House of Donghua University.

1.2 Instrument parameters of characterization

1.2.1 NMR of recovered BHET

Nuclear Magnetic Resonance Spectroscopy (NMR) including ^1H (600 MHz), $^{13}\text{C}\{^1\text{H}\}$ (151 MHz) were recorded at ambient temperature by using Bruker AVANCE III, HD 600 MHz spectrometers.

1.2.2 HPLC of recovered BHET

BHET purity test was carried out on American Waters high performance liquid chromatography. The chromatographic column was ACQUITY UPLC BEH C18 column (1.7 μm , 2.1 mm \times 100 mm). The mobile phase was acetonitrile-0.1% H_3PO_4 solution. The detection wavelength was 287nm. The column temperature was 35 $^\circ\text{C}$. The flow rate was 0.3 mL/min and the injection volume was 3 μL .

1.2.3 The chromaticity analysis on recovered BHET and recycled PET

The chromaticity (L^* , a^* , b^* value) test was carried out on the WSB-2 whiteness meter. The light source was D65. The angle was 10 $^\circ$. The whiteness index was the national standard GB/T17644. The measuring aperture was 4 mm in diameter and the resolution was 0.01.

1.2.4 The GPC of recycled PET and the textile samples

The molecular weight and molecular weight distribution of the polymers were measured on the Agilent PL-GPC50 gel permeation chromatography. The mobile phase was tetrahydrofuran and hexafluoroisopropanol with a flow rate of 1.0 mL/min. The standard sample was polystyrene.

1.2.5 The FT-IR analysis on recycled dyes

Fourier Transform Infrared Spectroscopy (FT-IR) were measured on Thermo Scientific Nicolet iS5.

1.2.6 The determination of decolorization rate

The decolorization rate of a textile was calculated with the following formula,

$$P = \frac{K_0 - K_1}{K_0} * 100\%$$

where P denotes the decolorization rate, K_0 denotes the K/S value of the original sample, and K_1 denotes the K/S value of the fabric after decolorization.

The K/S value was calculated with the Kubelka Munk's law¹,

$$K/S = \frac{[1 - 0.01R]^2}{2[0.01R]}$$

where R denotes the reverse color ratio of the object. R was measured on Shimadzu UV-3600 Ultraviolet-Visible-Near Infrared Spectroscopy by measuring the light reflectance R of the sample in the visible light wavelength range (380~750 nm). The scanning speed was medium. The sampling interval was 0.5 nm. The slit width was 20 nm and the detection unit was external (dual detector).

1.2.7 Computational Details

All the calculations were performed using Gaussian16 software packages. Geometry optimization uses the ω b97xd function with Grimme dispersion corrections D3 in combination with the def2tzvp basis set, which includes the solvation effects of experimentally used SMD solvation model (solvent=ethylene glycol). Vibrational frequency analysis was calculated at the same level of theory to validate each structure as either a minimum or a transition state and to evaluate its zero-point energy and thermal corrections at 298 K. For the transition state, the intrinsic reaction coordinate (IRC) analysis was conducted to ensure that it connects the right reactant and product. The heat of vaporization (ΔH_{vap}) of BHET melt², heat of sublimation (ΔH_{sub}) of BHET powder² and the enthalpy of transition state of the condensation reaction ($\Delta H_{\text{polym.}}$)³ were calculated using the parameters listed in the literatures.

2. Chemical reactions

2.1 The glycolysis reaction of polyester materials

2.1.1 The glycolysis reaction of pure PET and the purification of BHET

The glycolysis reaction was carried out in a 100 mL round-bottom flask, which was connected to a condenser. A mixture of a PET sample (2 g), potassium carbonate (0.04 g, 2 wt%) and ethylene glycol (12 g, a mass ratio of PET to ethylene glycol is 1:6) was heated at 250 °C for 2.5h. After reaction, the solution was let to slowly cool down to room temperature (8~12°C) to afford BHET crystals. The crystals were quickly filtered under reduced pressure. The mother liquor was concentrated under reduced pressure to approximately a half volume, and was heated to 190 °C until a clear solution was obtained. The solution was then let to slowly cool down to room temperature (8~12°C) to allow a second recrystallization. The crystalline BHET obtained was

combined with the previous portion. The combined crystals were sublimated under reduced pressure (1.33 kPa) at 135 °C with a glass sublimation setup to afford purified BHET in solid state (2.286 g, 86.4% yield). The product BHET was characterized by ¹H NMR, HPLC and chromaticity test.

2.1.2 The decolorization of waste polyester textile

The textile sample was cut into a size of approximately 5×5 cm² and then hung above the surface of a boiling steam of ethylene glycol in a 100 mL round-bottom flask, which was connected with a condenser. After the color did not change, the textile sample was taken out from the flask and washed with ethanol to remove ethylene glycol sucked by the textile. The decolorized textile was then subjected a vacuum for 5 min to completely remove ethanol.

Gel permeation chromatography (GPC) analysis was applied to monitor the changes of the PET molecules of the textile during the decolorization process. Fig. S1 shows the GPC results of the polyester textile sample before and after decolorization treatment.

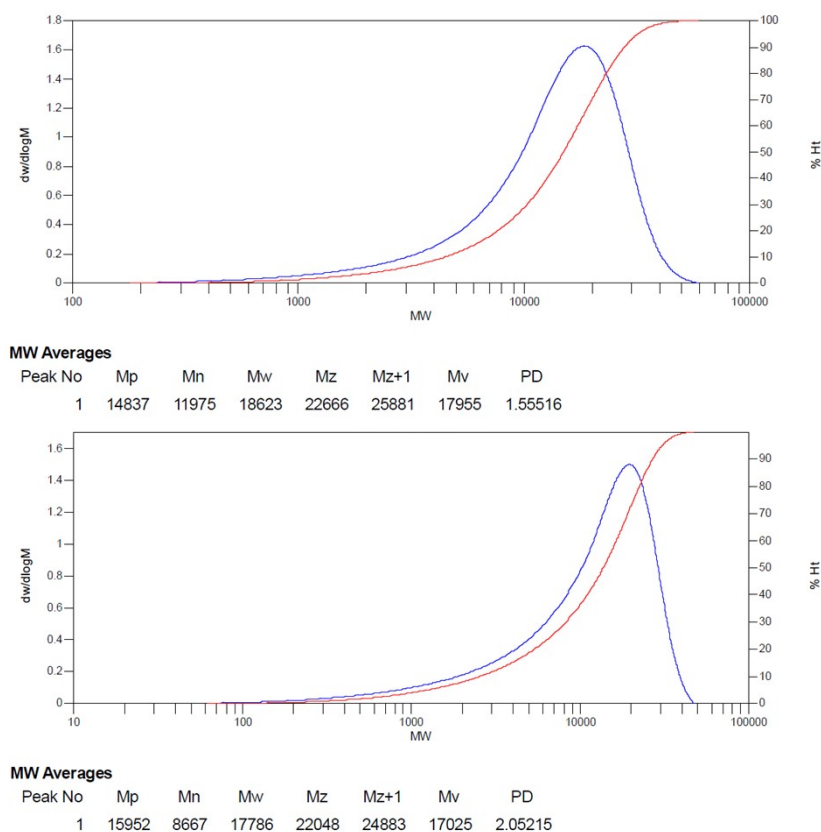


Fig. S1 The GPC spectra of a polyester textile sample before decolorization (above) and after a decolorization treatment with ethylene glycol steam in 10 min (below).

2.1.3 The glycolysis reaction of decolorized textile and the purification of BHET

The same procedure for the glycolysis of pure PET and purification of product BHET was used with the decolorized textile sample.

2.2 The polycondensation of BHET to produce recycled PET

2.2.1 The polycondensation of commercial BHET

A two-stage condensation procedure for the polycondensation of BHET to synthesize recycled PET (r-PET) was employed, including a pre-condensation at 250 °C for 1h and a final condensation at 280 °C for 1h. In a 5 mL round-bottom flask that was charged with a stirring bar, BHET (0.7 g) and ethylene glycol antimony (200 ppm) was heated at 250 °C and 1.33 kPa pressure with stirring for 1h. Then the temperature was slowly raised to 280 °C in a period of 10 min. The mixture was further heated at 280 °C and 1.33 kPa pressure with stirring for 1h. After the completion of polycondensation reaction, the flask was slowly cooled to room temperature under a nitrogen atmosphere. The PET obtained was characterized by GPC and chromaticity tests.

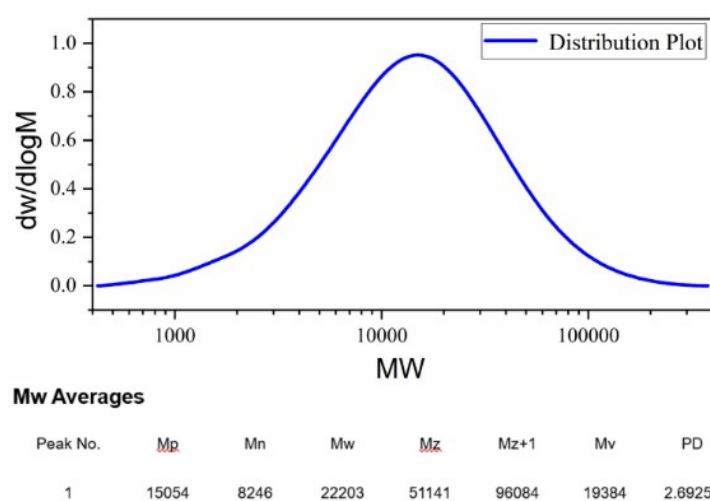
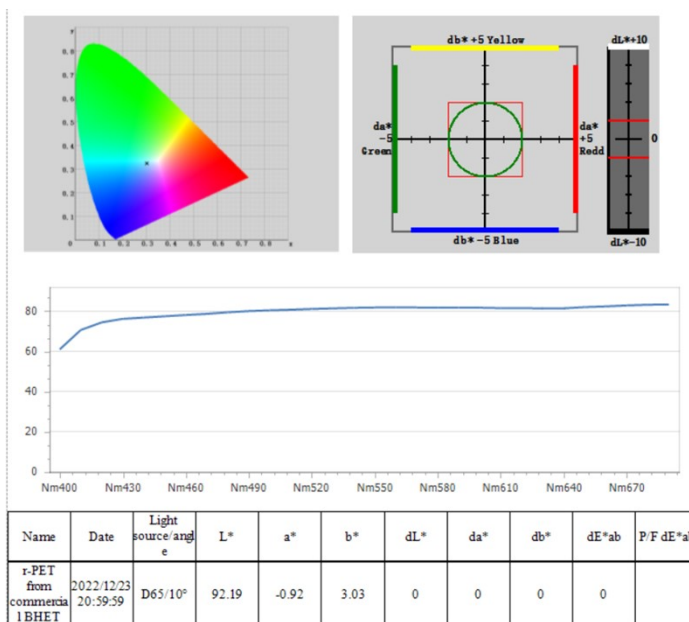
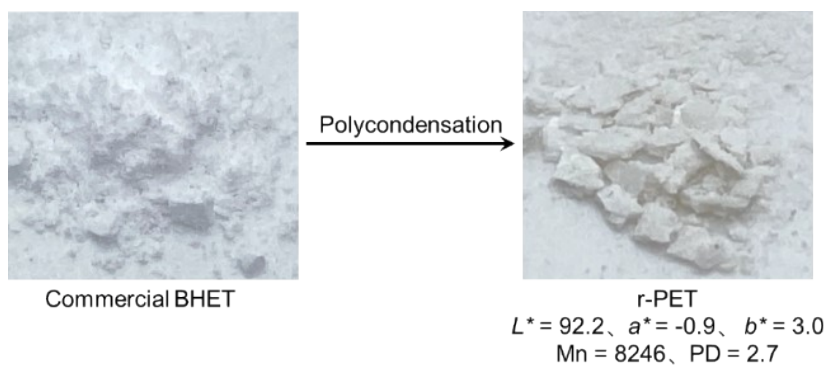


Fig. S2 the photograph, chromaticity and GPC results of r-PET derived from commercial BHET.

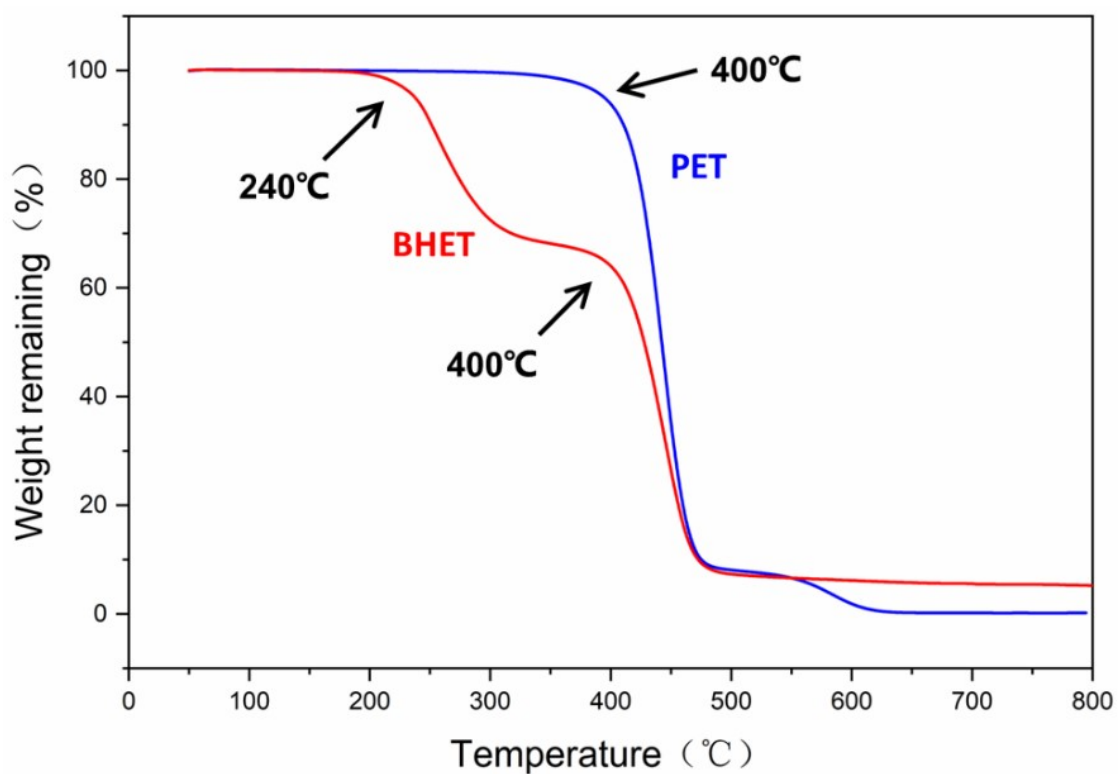


Fig. S3 The thermogravimetric analyses (TGA) spectra of commercial BHET (red) and PET (blue) produced by polycondensation of BHET. TGA8000 (PerkinElmer) was conducted in a nitrogen atmosphere during a temperature range from 50 °C to 800 °C at a heating rate of 20 °C /min.

2.2.2 The polycondensation of recovered BHET from waste polyester textiles

The same procedure for the polycondensation of commercial BHET was used in the polycondensation of recovered BHET from waste polyester textiles.

2.2.2.1 The properties of recycled PET derived from BHET sample 8

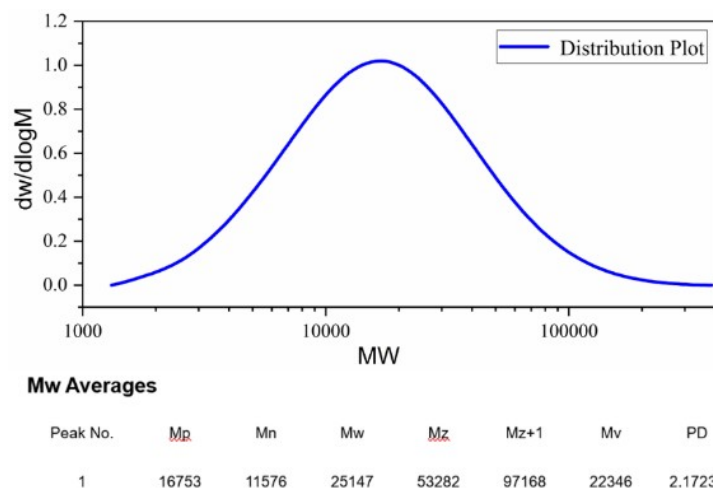
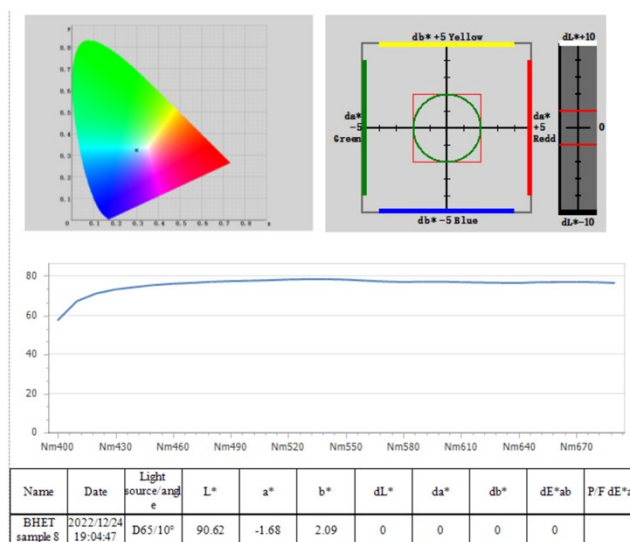
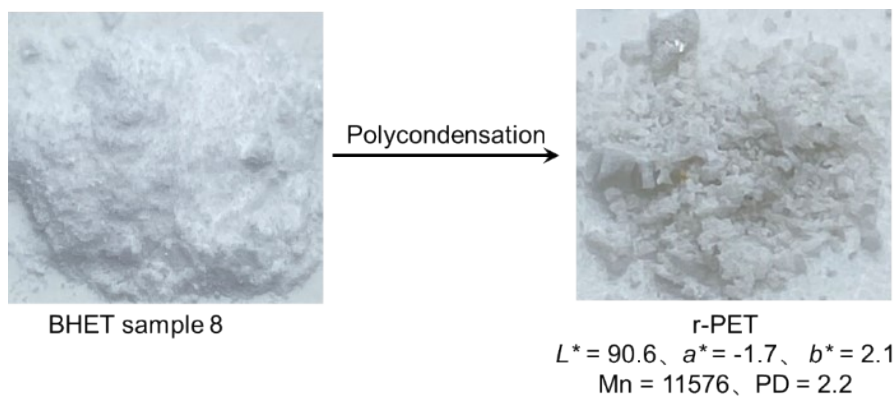
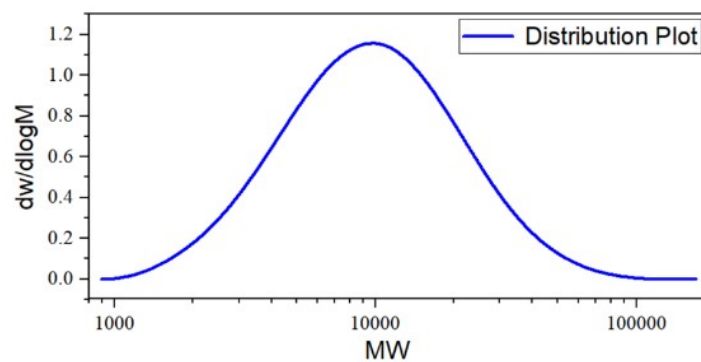
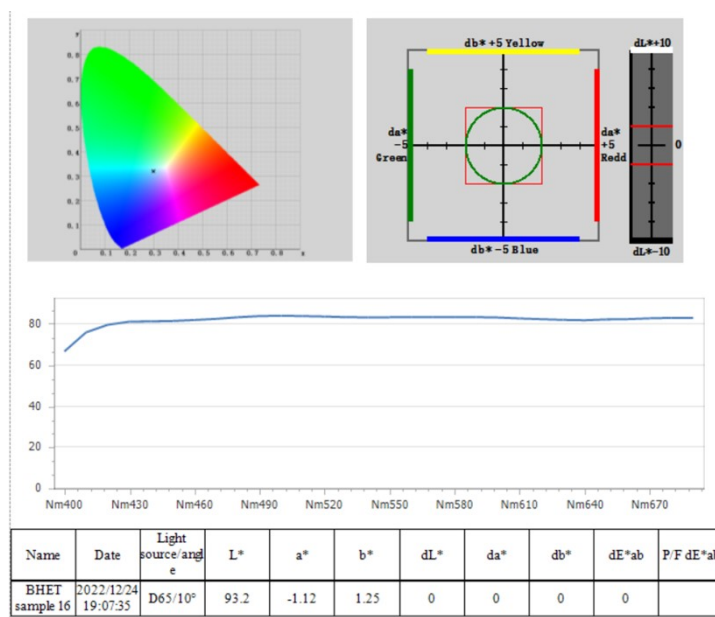
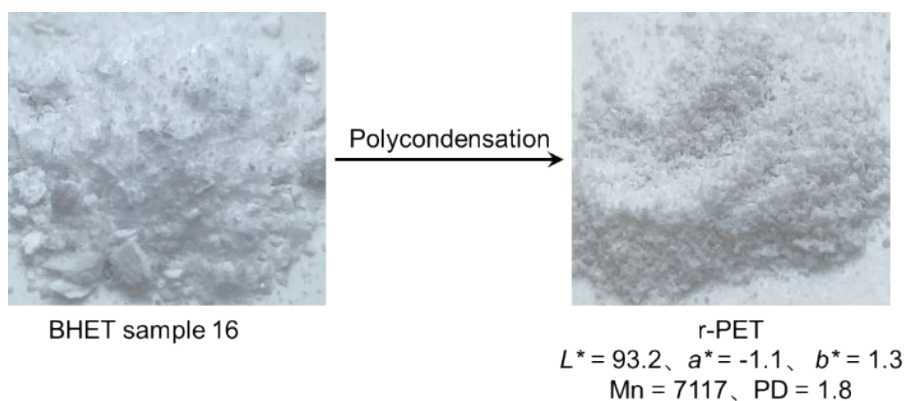


Fig. S4 the photograph, chromaticity and GPC results of r-PET derived from recovered BHET (sample 8).

2.2.2.2 The properties of recycled PET derived from BHET sample 16



Mw Averages

Peak No.	M_p	M_n	M_w	M_z	M_{z+1}	M_v	PD
1	9816	7117	12773	22014	34145	11713	1.79472

Fig. S5 the photograph, chromaticity and GPC results of r-PET derived from recovered BHET (sample16).

2.2.2.3 The properties of recycled PET derived from BHET sample 23

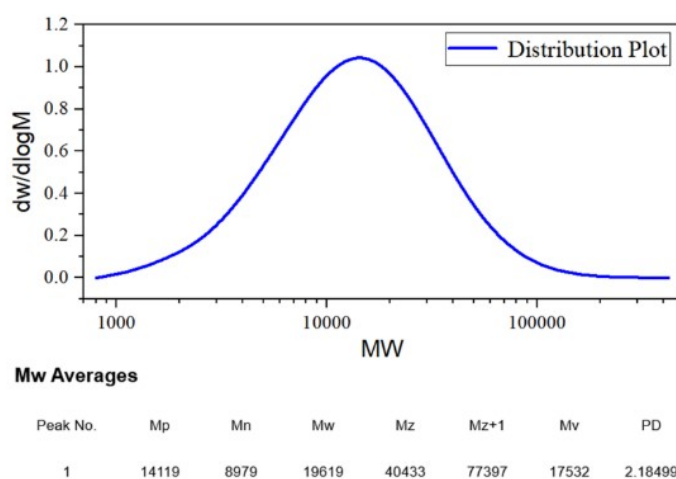
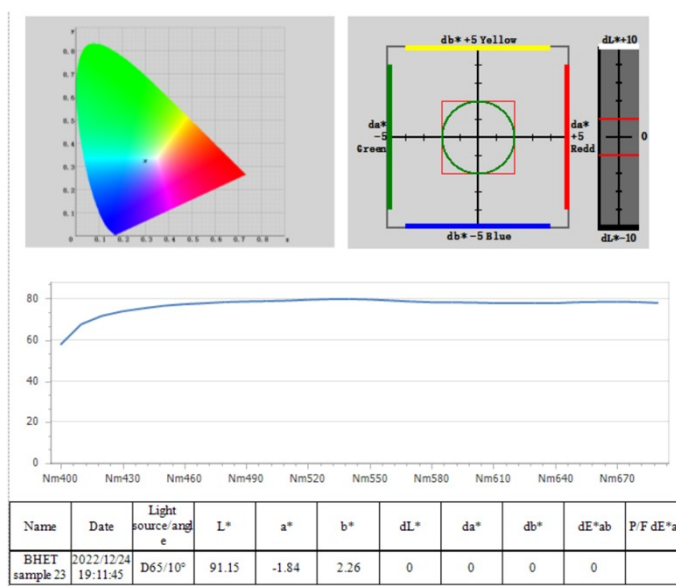
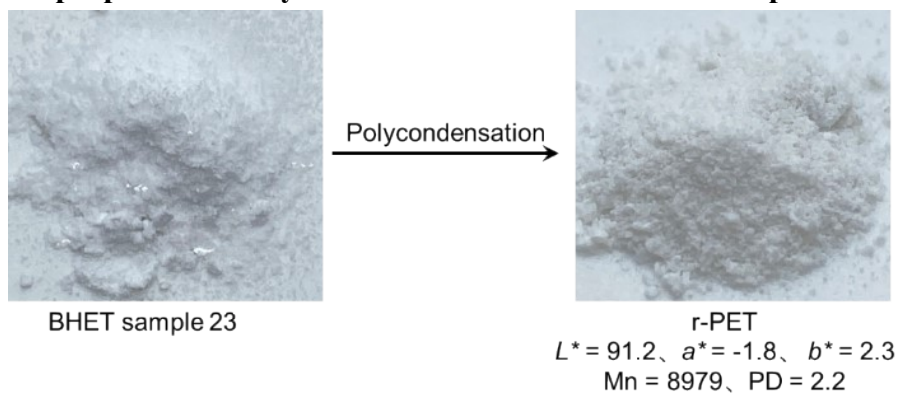


Fig. S6 the photograph, chromaticity and GPC results of r-PET derived from recovered BHET (sample 23).

2.2.2.4 The properties of recycled PET derived from BHET sample 37

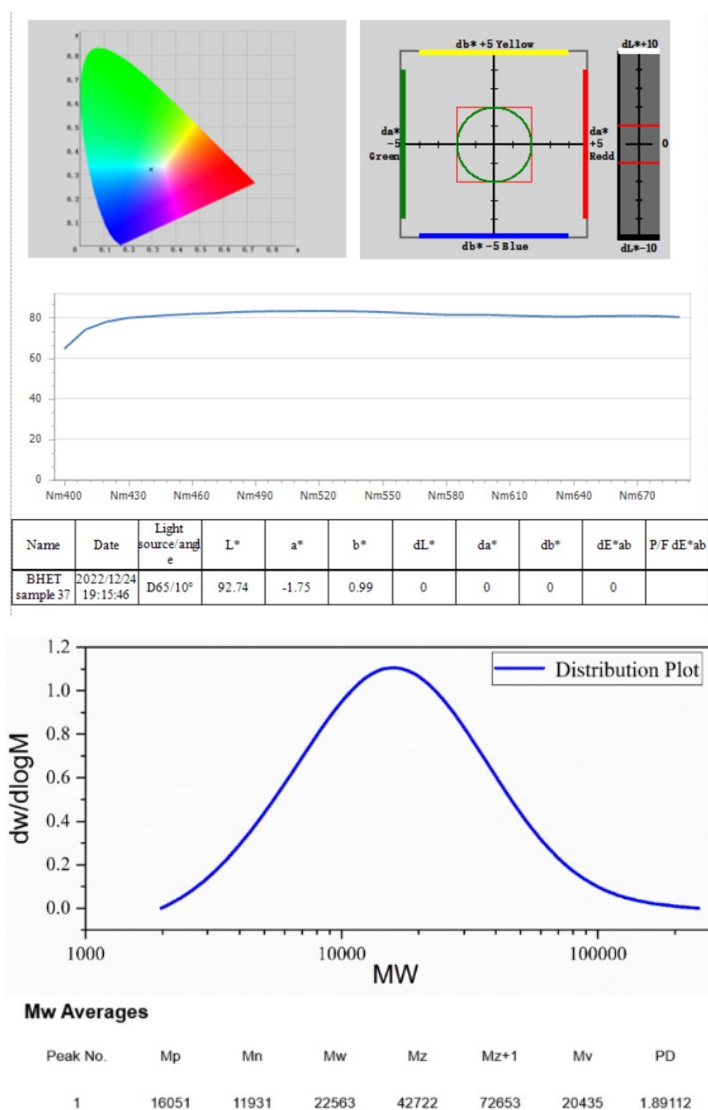
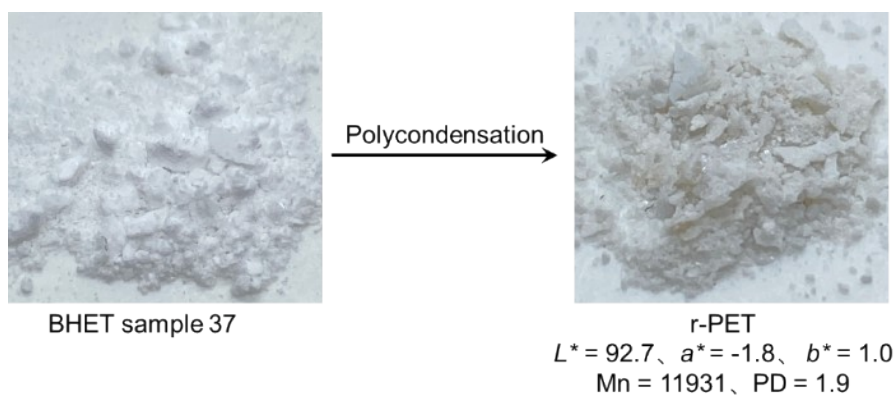


Fig. S7 the photograph, chromaticity and GPC results of r-PET derived from recovered BHET (sample 37).

2.2.2.5 The properties of recycled PET derived from BHET sample 48

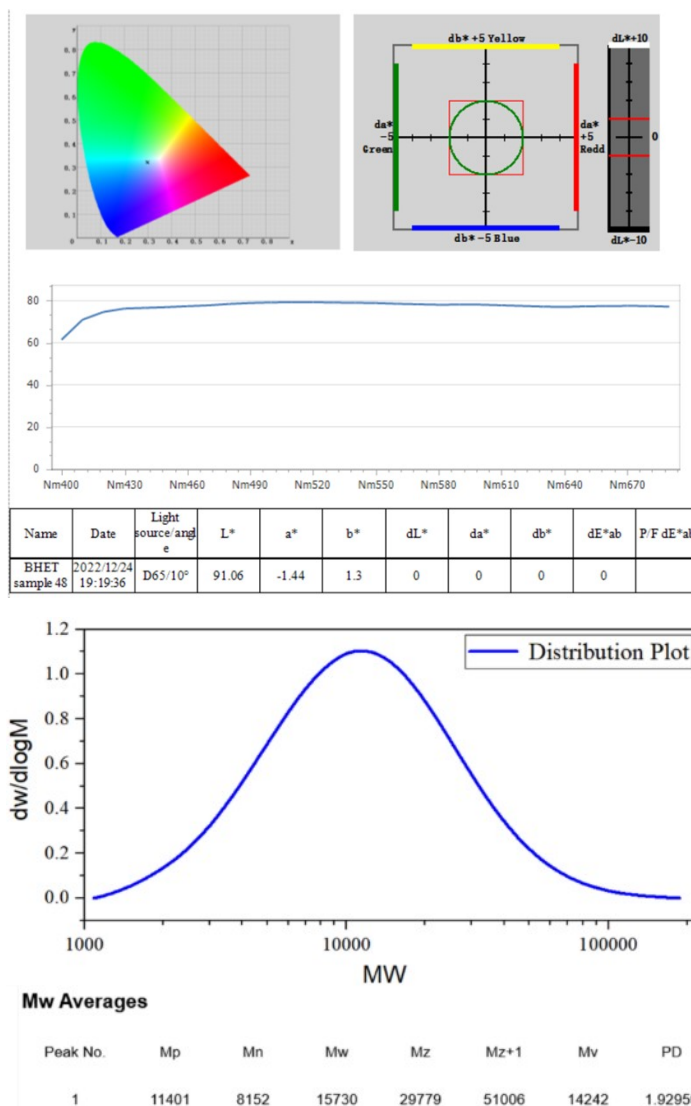
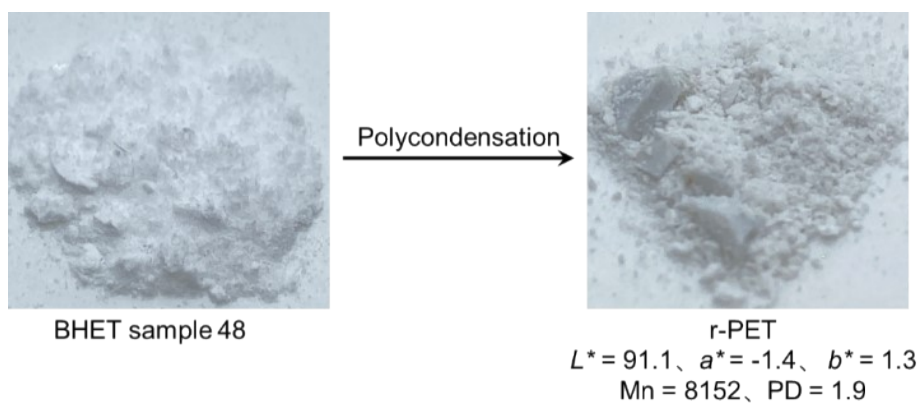
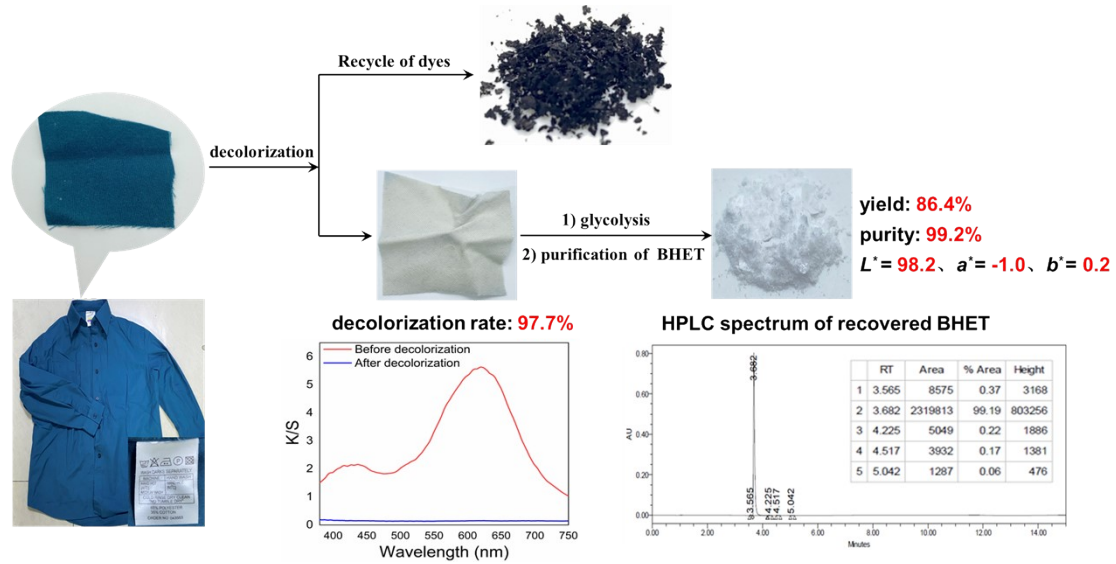


Fig. S8 the photograph, chromaticity and GPC results of r-PET derived from recovered BHET (sample 48).

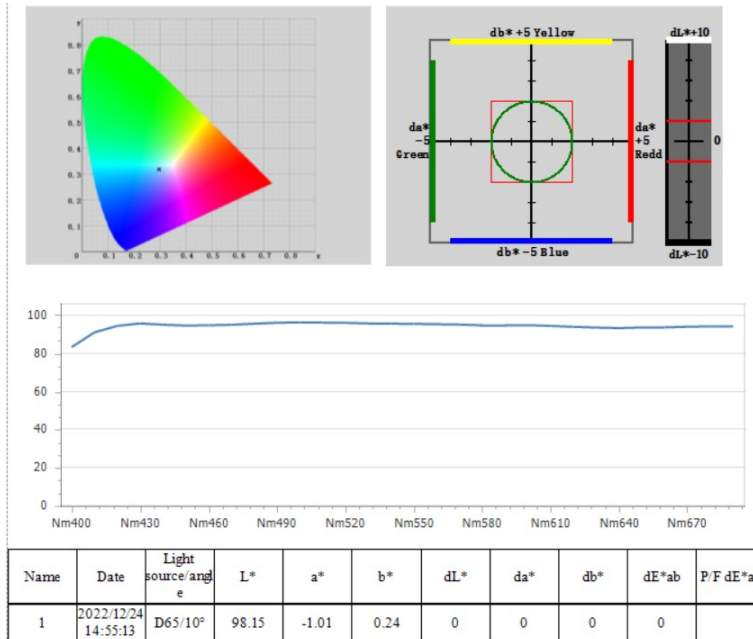
3. The decolorization of waste polyester textiles, the recycling of dyes and the recovery of BHET

3.1 Sample 1

Composition: 65% Polyester, 35% Cotton



Chromaticity of recovered BHET:



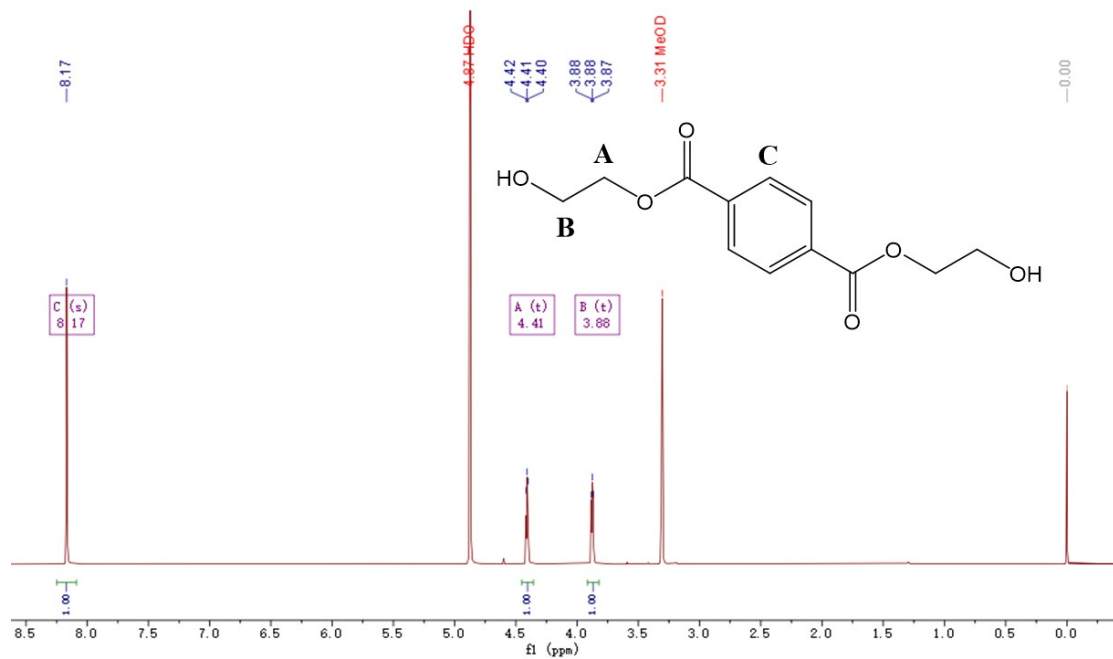


Fig. S9 The ^1H NMR (600 MHz, *d4*-methanol) of recovered BHET.

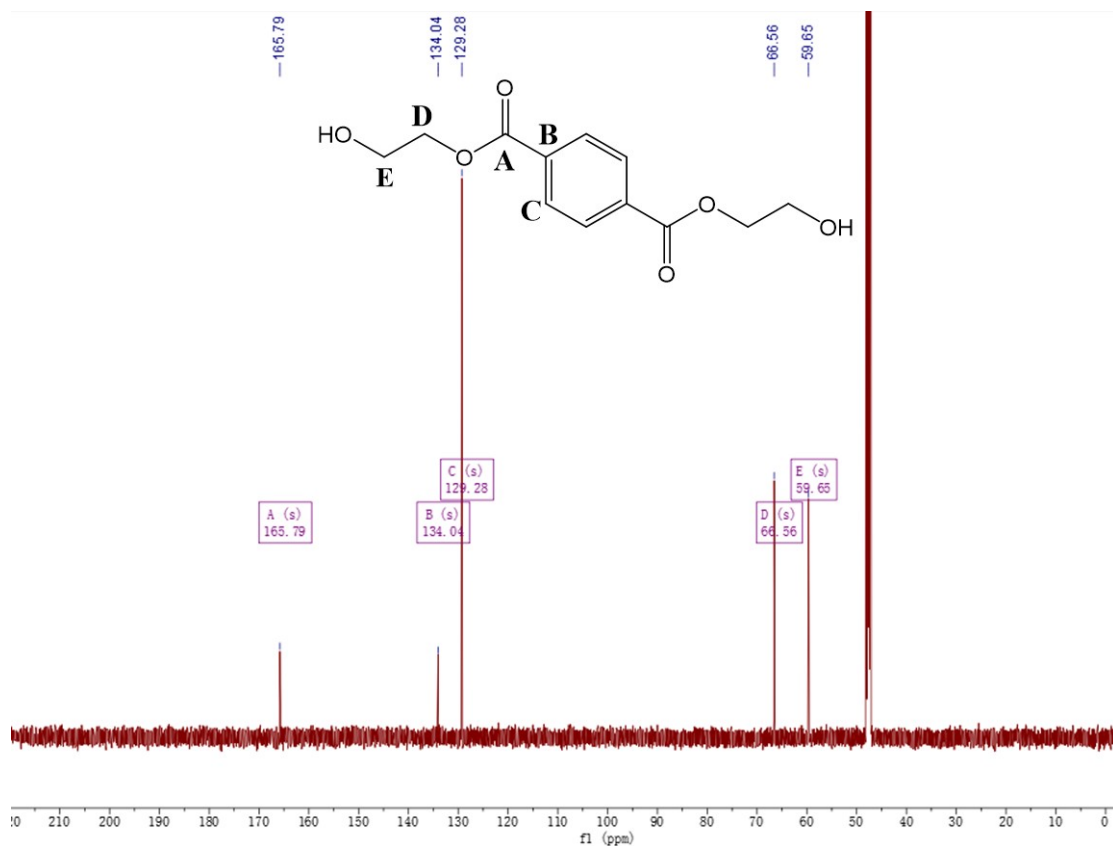


Fig. S10 The ^{13}C NMR (151 MHz, *d4*-methanol) of recovered BHET.

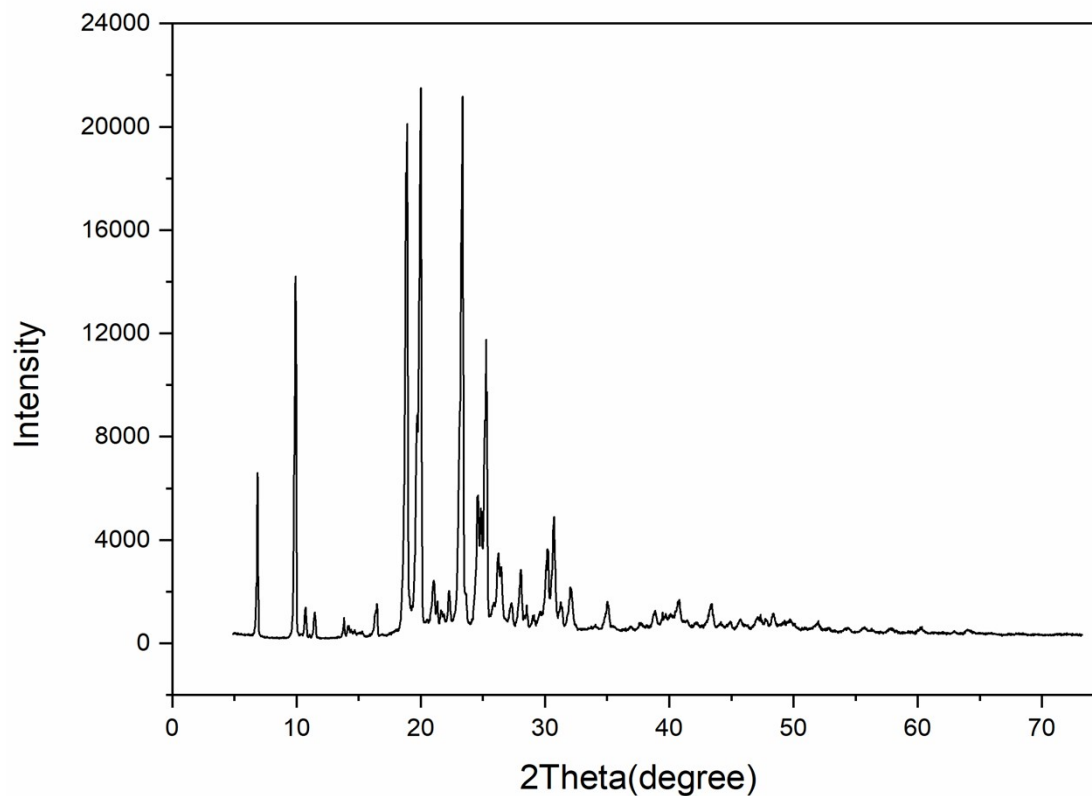


Fig. S11 The X-ray diffraction (XRD) spectrum of recovered BHET. X-ray diffraction (XRD) pattern of BHET was recorded in the range $2\theta = 5-75^\circ$ using an X-ray Powder diffractometer (Bruker D8 Discover) with Cu $K\alpha$ radiation ($\lambda = 0.154$ nm). The instrument was operated at 40 kV and 40 mA. The spectra were recorded at a scanning rate of $2^\circ \theta/\text{min}$.

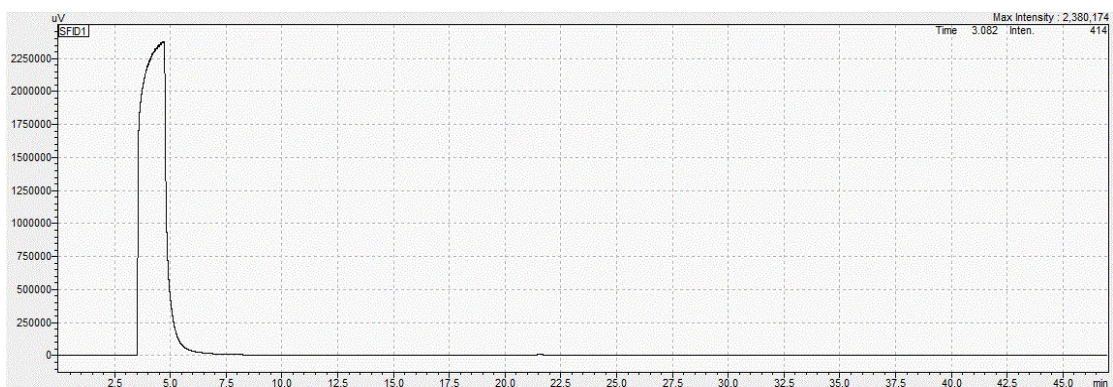


Fig. S12 The gas chromatography (GC) spectra of fresh ethylene glycol, ethylene glycol that was distilled after 6 recycles of glycolysis reaction and ethylene glycol, which was distilled after decolorization of sample 1. The characterization conditions: InertCap CHRAMIX, 30m×0.25mm, $df = 2.5\mu\text{m}$, nitrogen gas as a mobile phase at a column pressure of 5 psi. The injector and the FID temperatures were 275 °C. The column oven temperature procedure: 90 °C for 15min, 5 °C /min to 150 °C for 20 minutes.

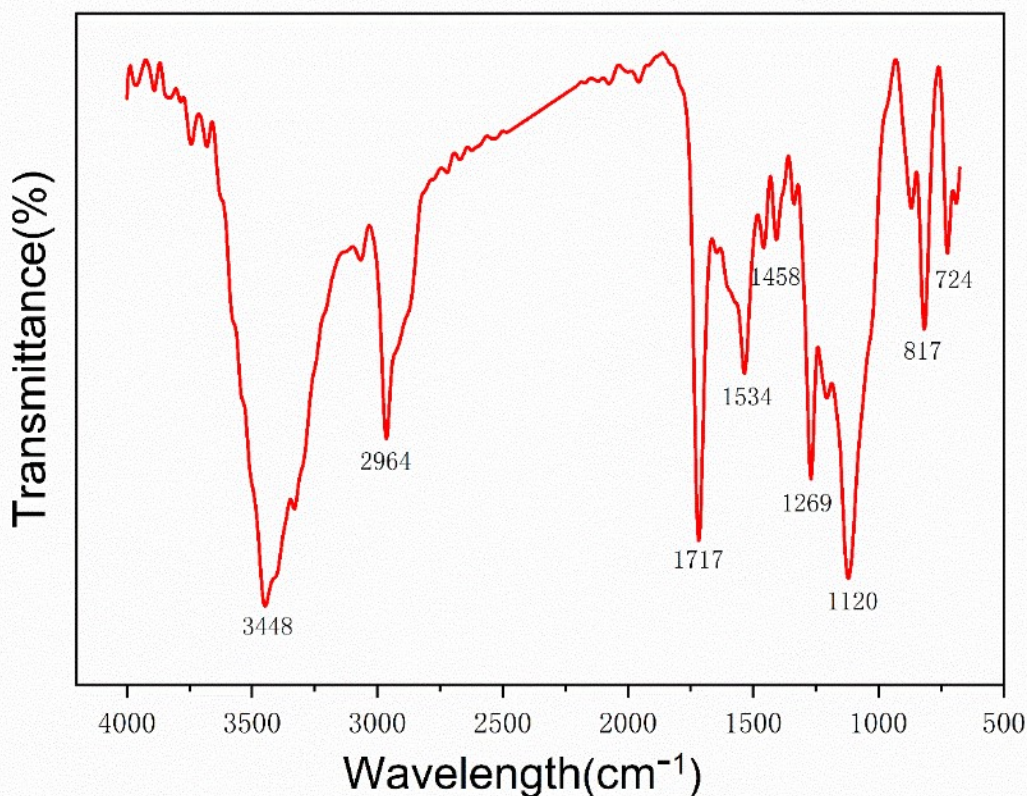


Fig. S13 The Fourier Transform Infrared Spectroscopy (FT-IR) spectra of recovered dye from textile **Sample 1**. The 1717 cm^{-1} peak corresponds to the C=O stretching and the signals at 1269 and 1120 cm^{-1} are the corresponding C-O-C asymmetric and symmetric stretching vibrations. 1534 cm^{-1} was assigned to N=O stretching vibration of the nitro group. The peaks at 724 , 817 , 1450 - 1600 cm^{-1} were attributed to substituted aryl groups. The potential molecule structures of this recovered dye were shown in **Fig. S14**.

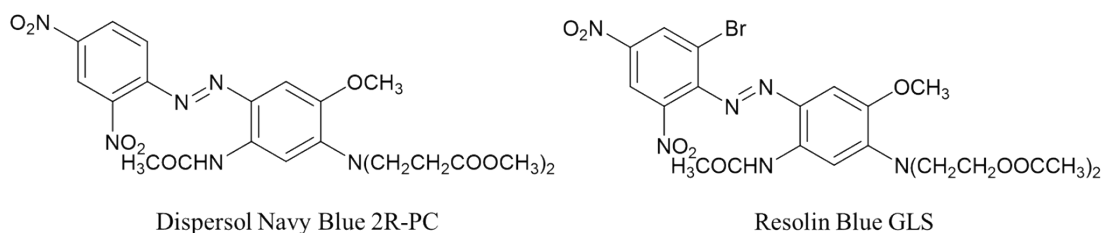
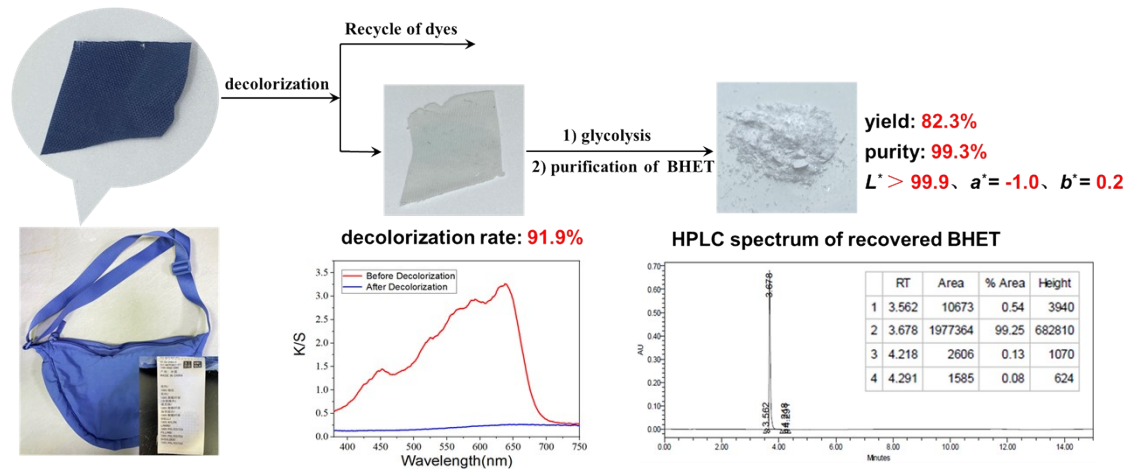


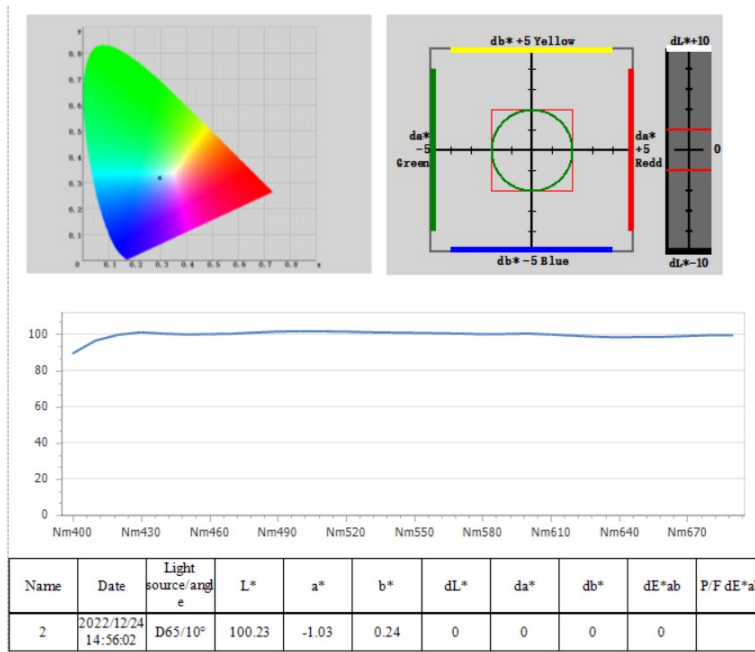
Fig. S14 The potential molecule structure of the recovered dye from textile **Sample 1**.

3.2 Sample 2

Composition: 100% Polyester

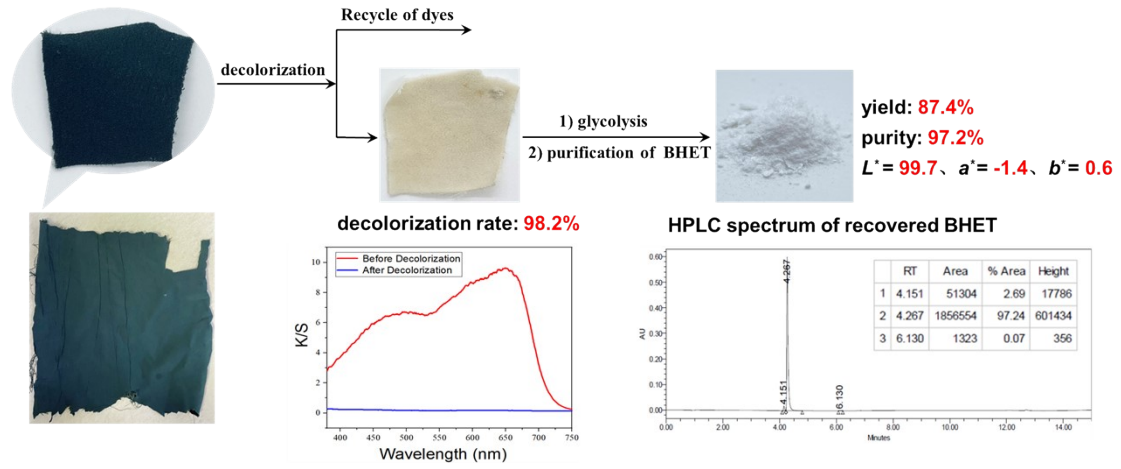


Chromaticity of recovered BHET:

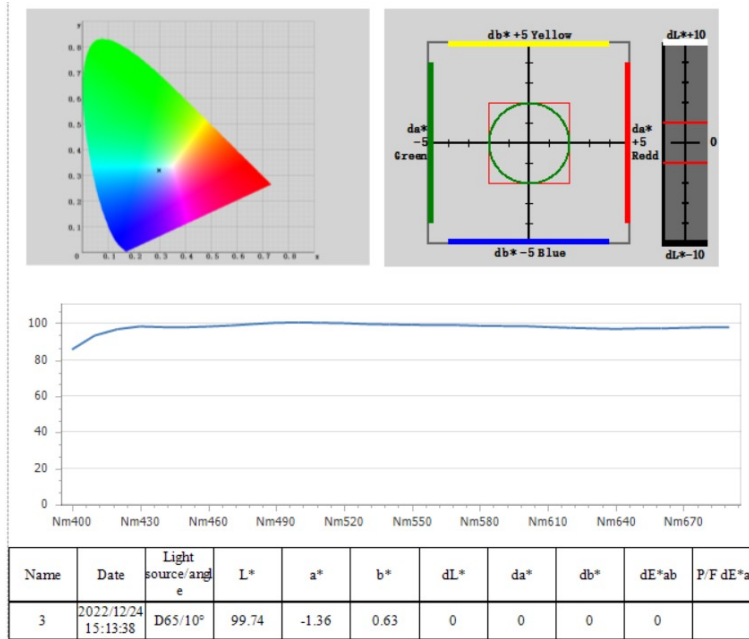


3.3 Sample 3

Composition: 85% Polyester, 15% Spandex

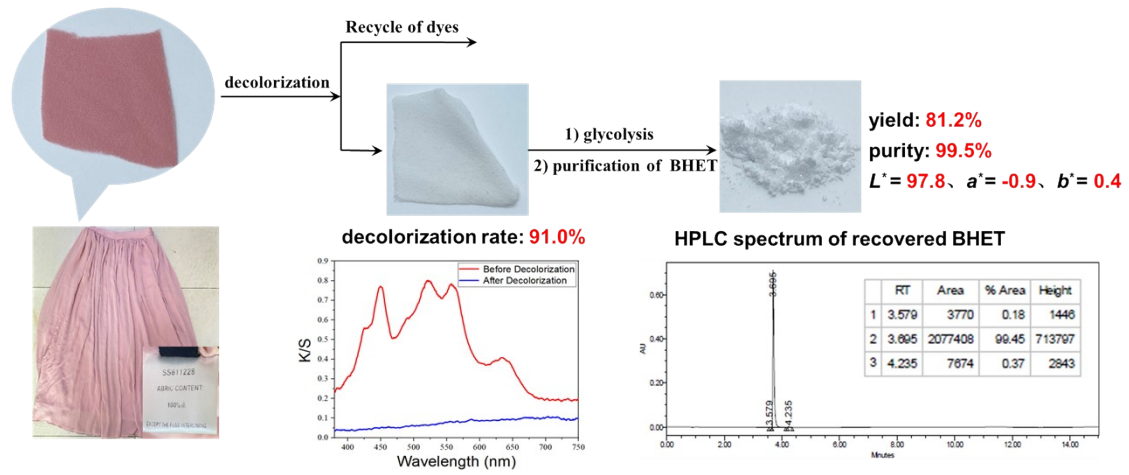


Chromaticity of recovered BHET:

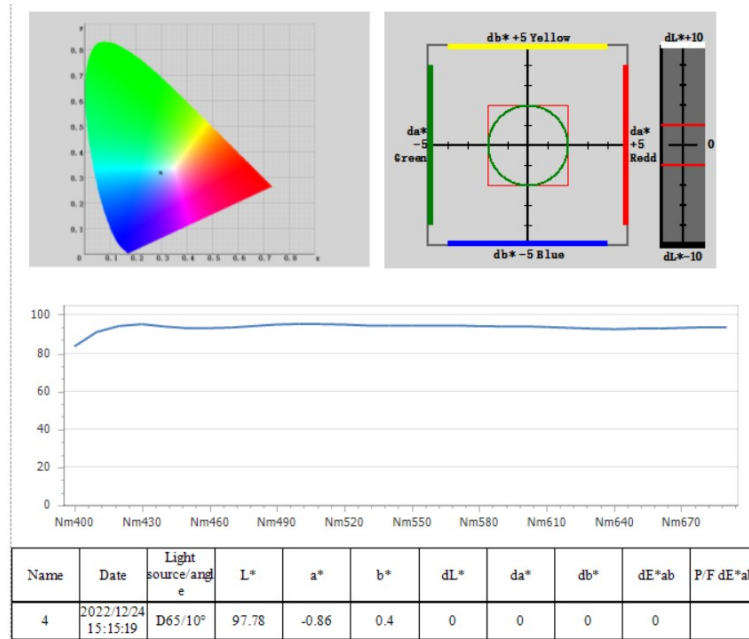


3.4 Sample 4

Composition: 100% Polyester

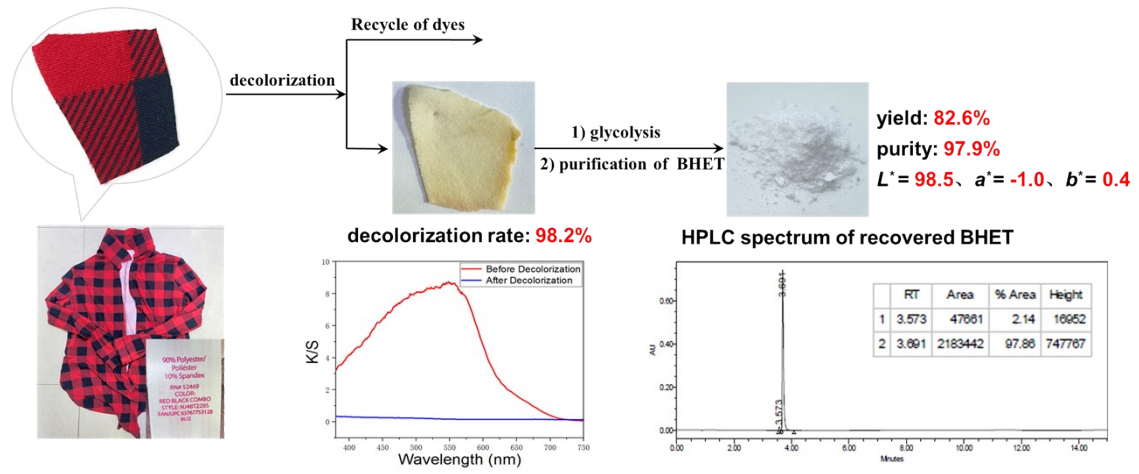


Chromaticity of recovered BHET:

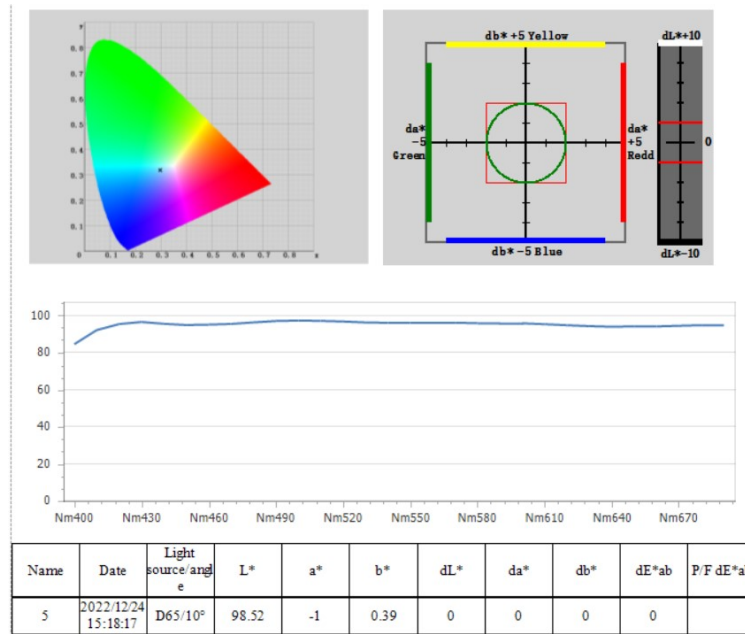


3.5 Sample 5

Composition: 90% Polyester, 10% Spandex

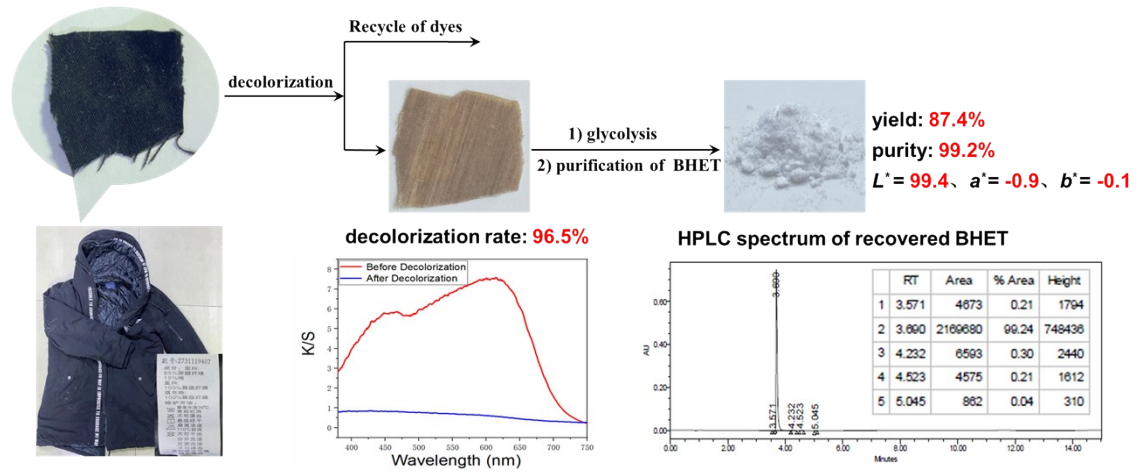


Chromaticity of recovered BHET:

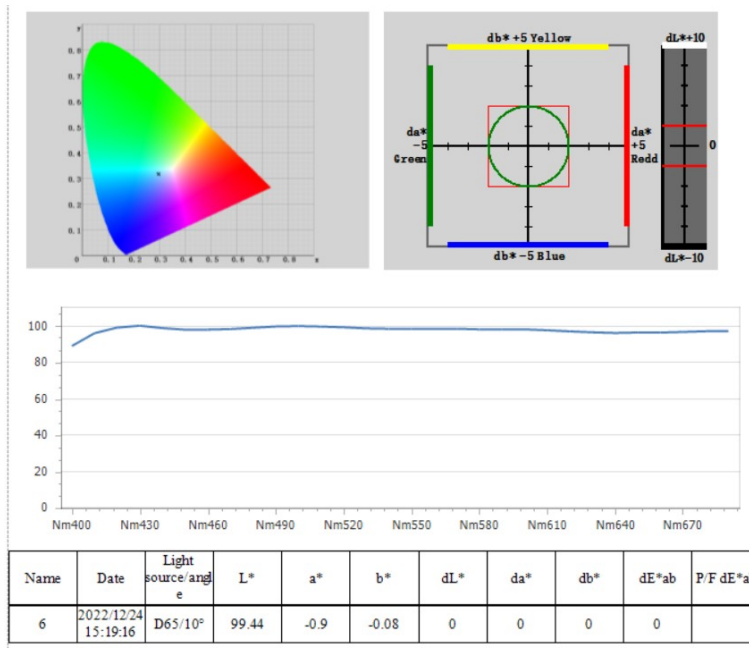


3.6 Sample 6

Composition: 85% Polyester, 15% Cotton

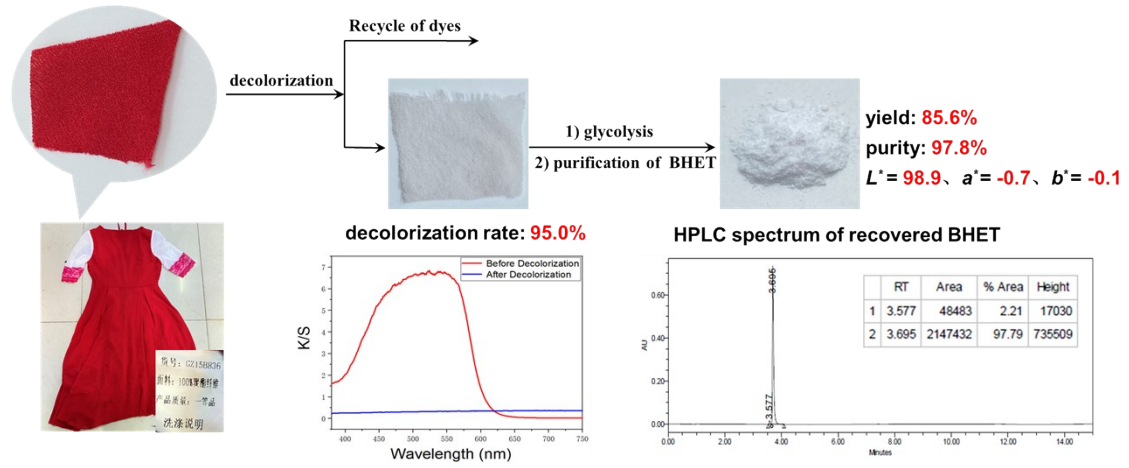


Chromaticity of recovered BHET:

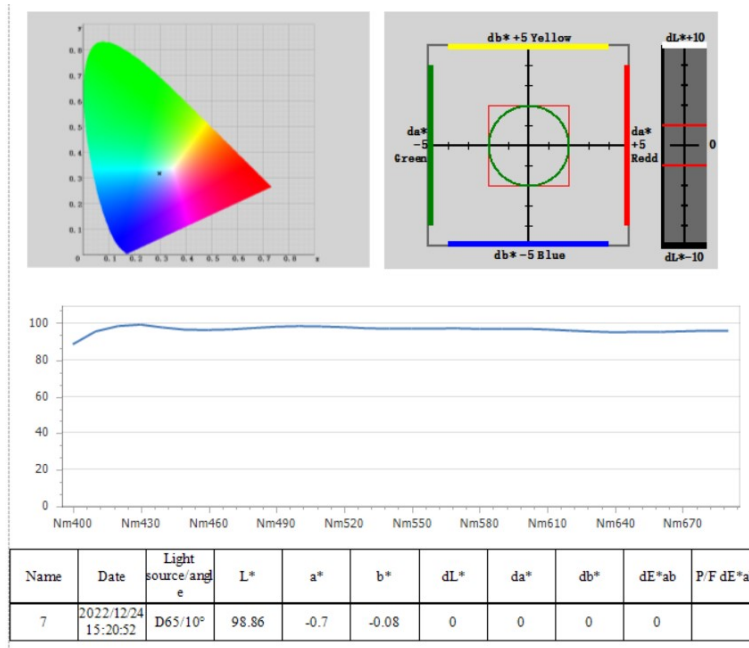


3.7 Sample 7

Composition: 100% Polyester

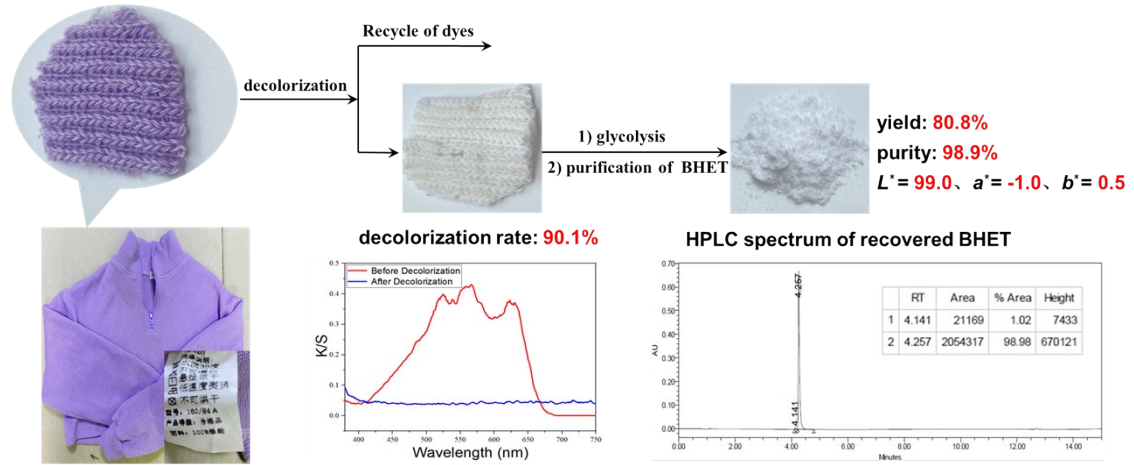


Chromaticity of recovered BHET:

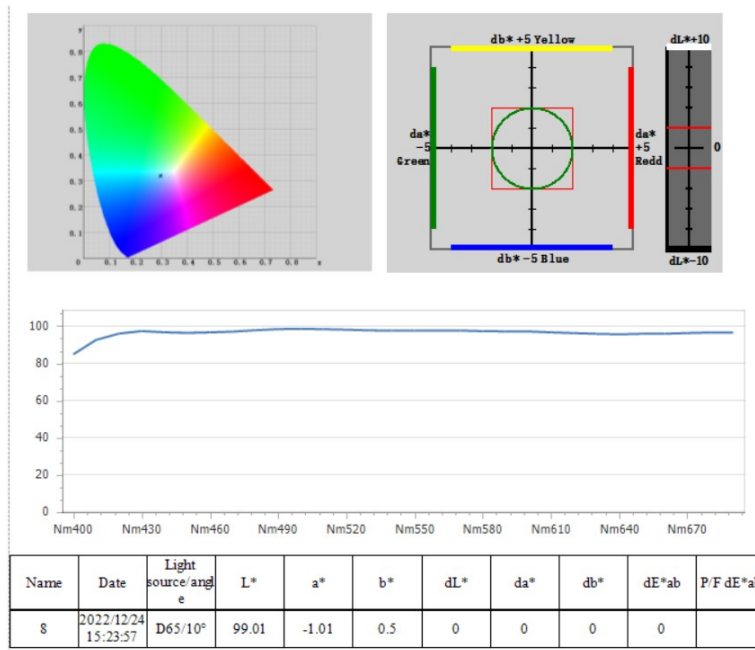


3.8 Sample 8

Composition: 100% Polyester

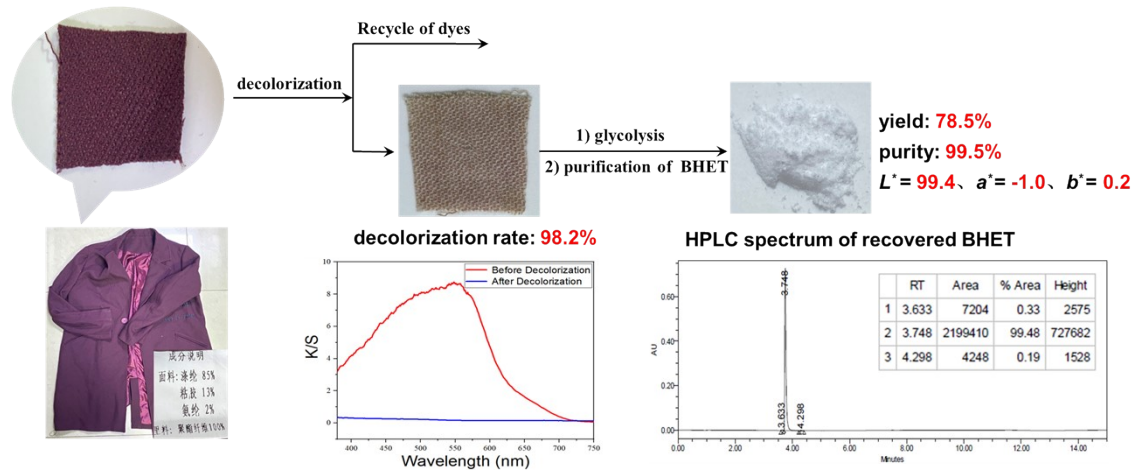


Chromaticity of recovered BHET:

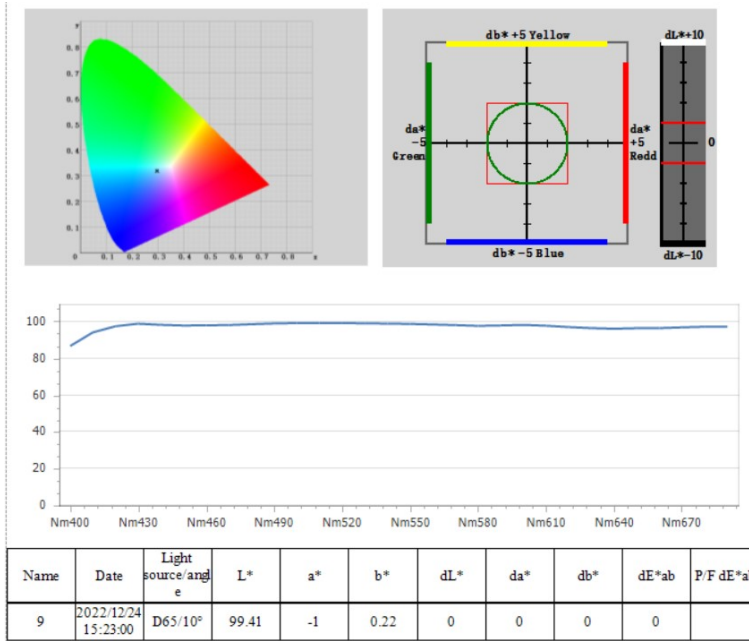


3.9 Sample 9

Composition: 85% Polyester、13% Viscose、2% Spandex

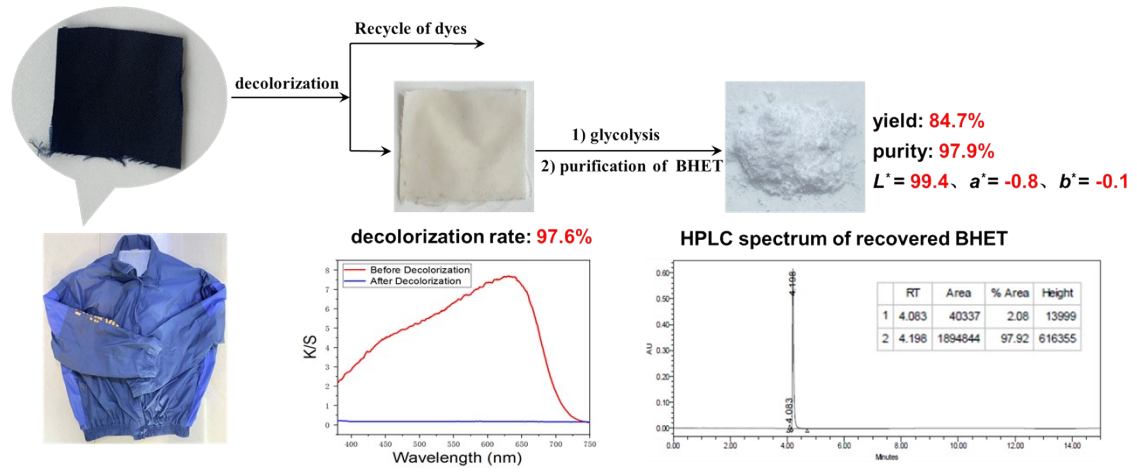


Chromaticity of recovered BHET:

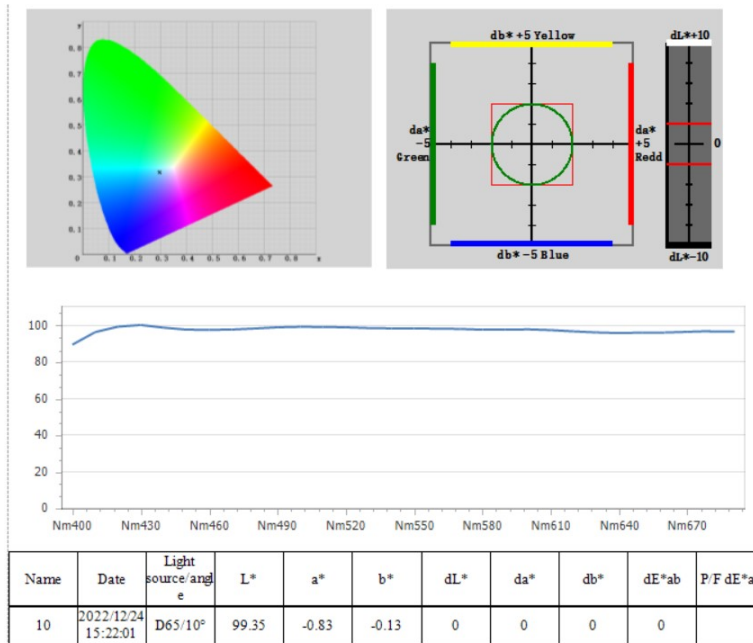


3.10 Sample 10

Composition: 100% Polyester

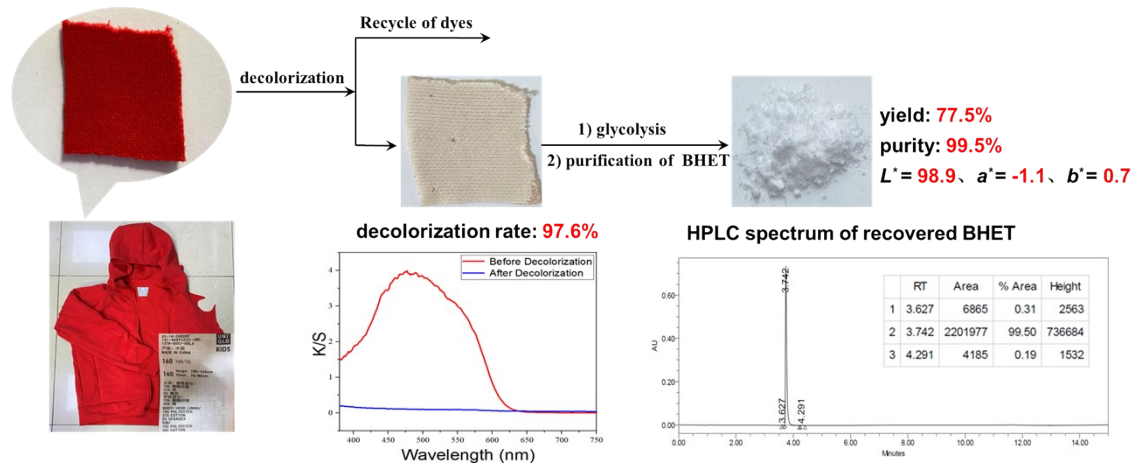


Chromaticity of recovered BHET:

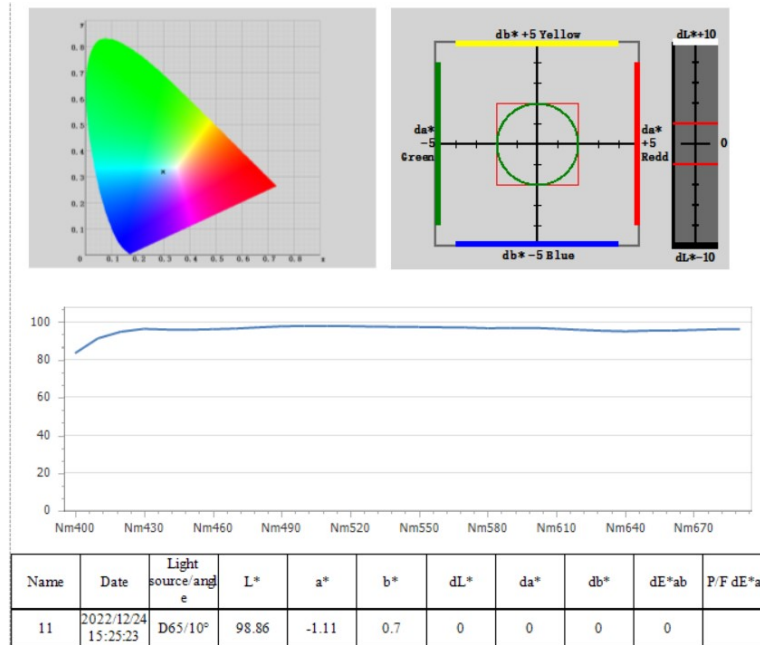


3.11 Sample 11

Composition: 74% Polyester, 21% Cotton, 5% Spandex

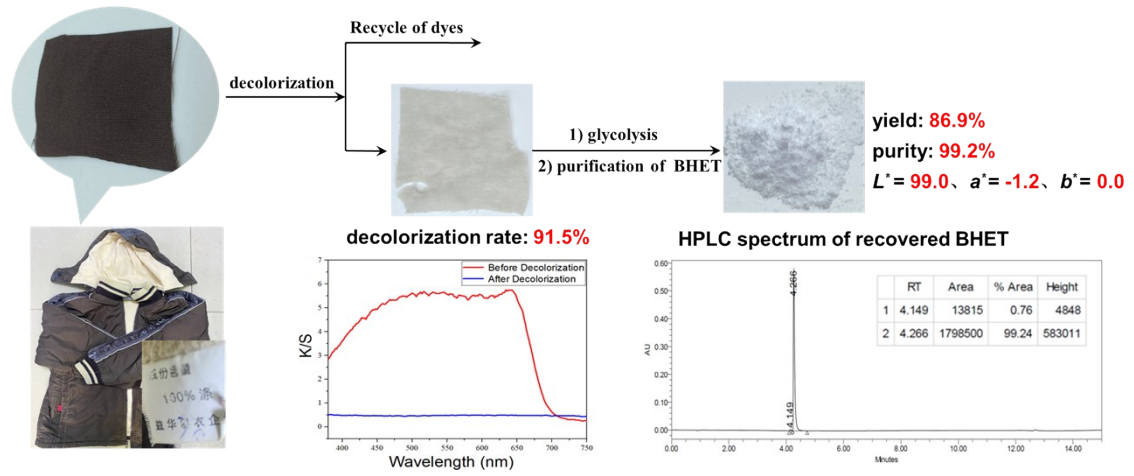


Chromaticity of recovered BHET:

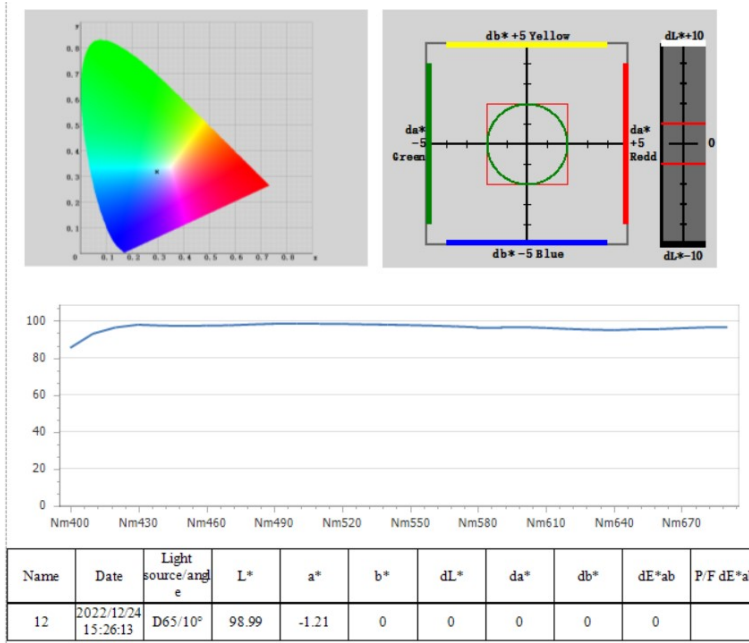


3.12 Sample 12

Composition: 100% Polyester

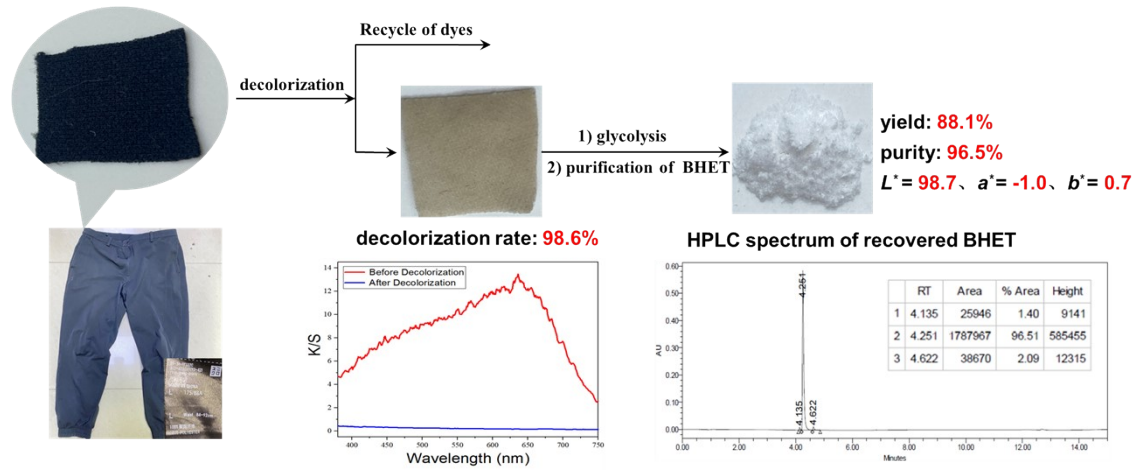


Chromaticity of recovered BHET:

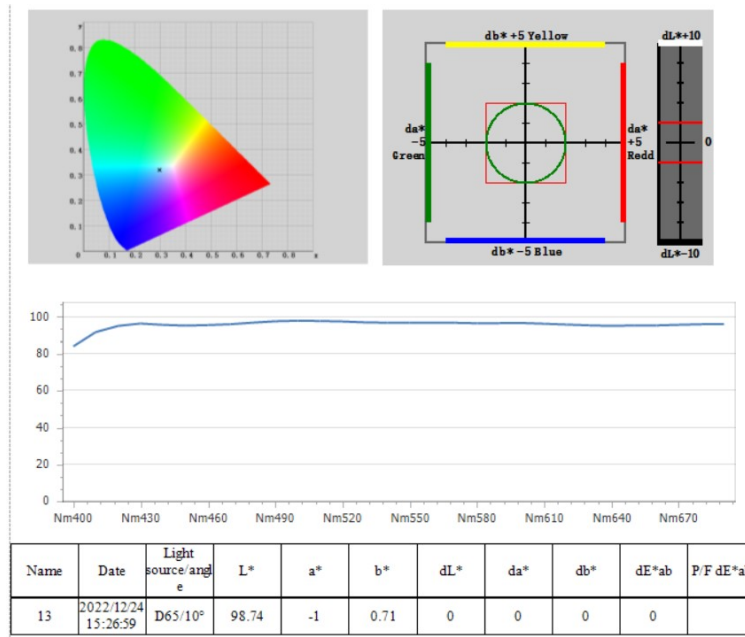


3.13 Sample 13

Composition: 100% Polyester

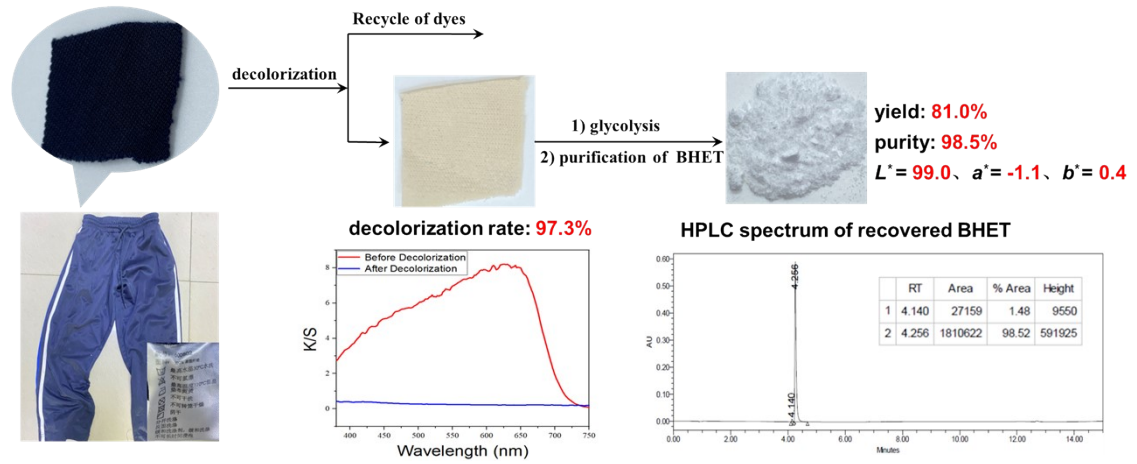


Chromaticity of recovered BHET:

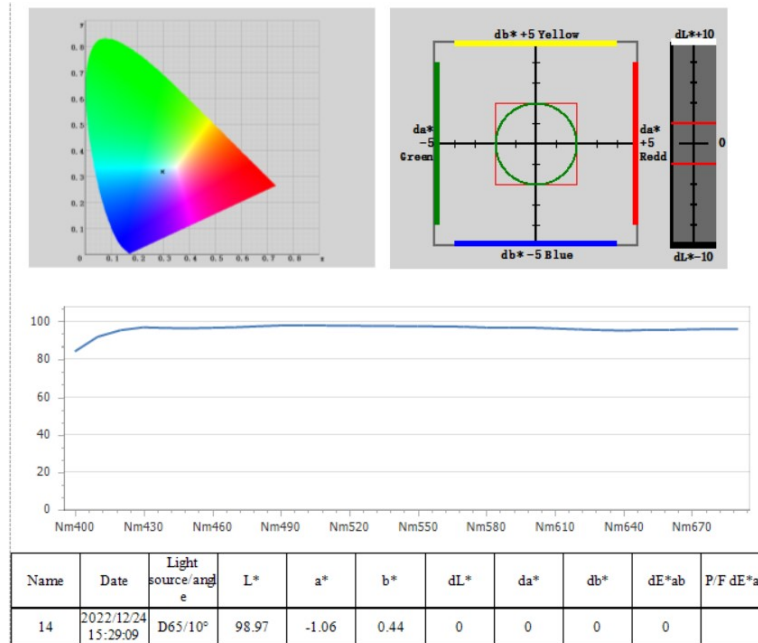


3.14 Sample 14

Composition: 100% Polyester

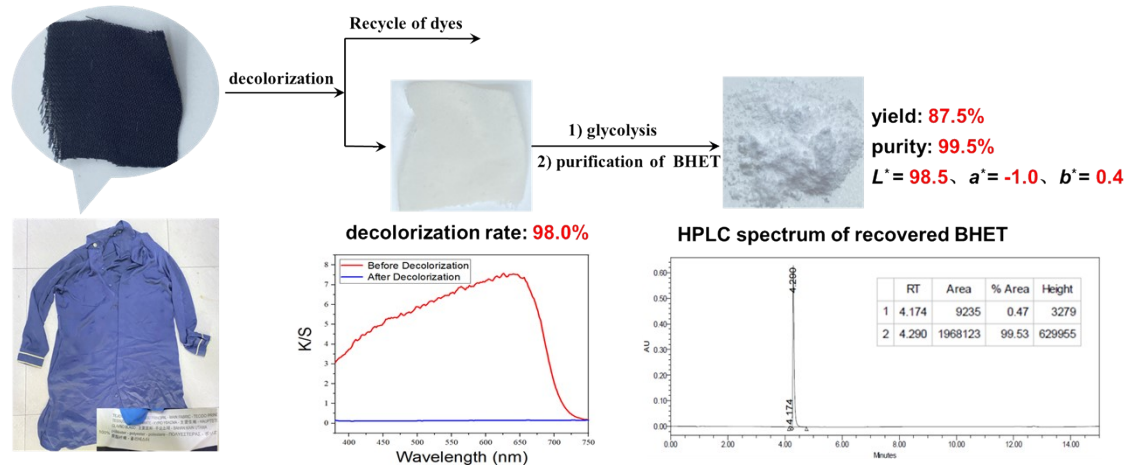


Chromaticity of recovered BHET:

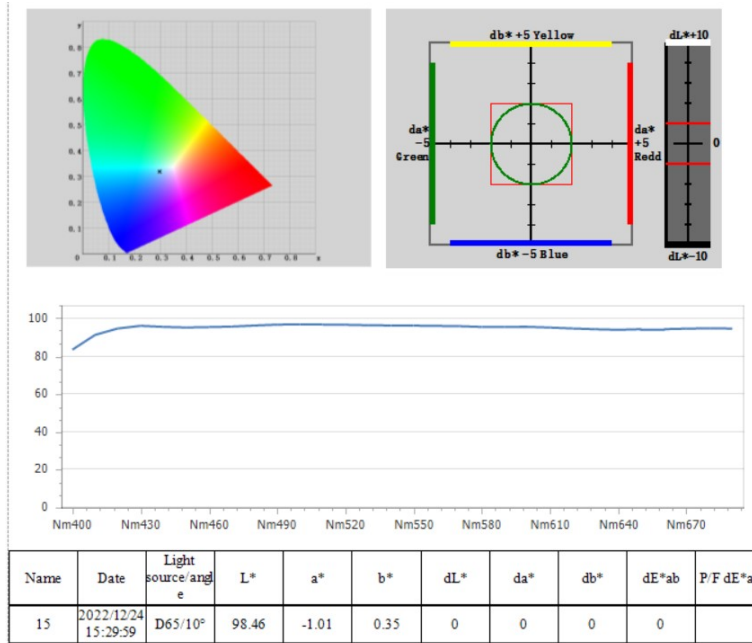


3.15 Sample 15

Composition: 100% Polyester

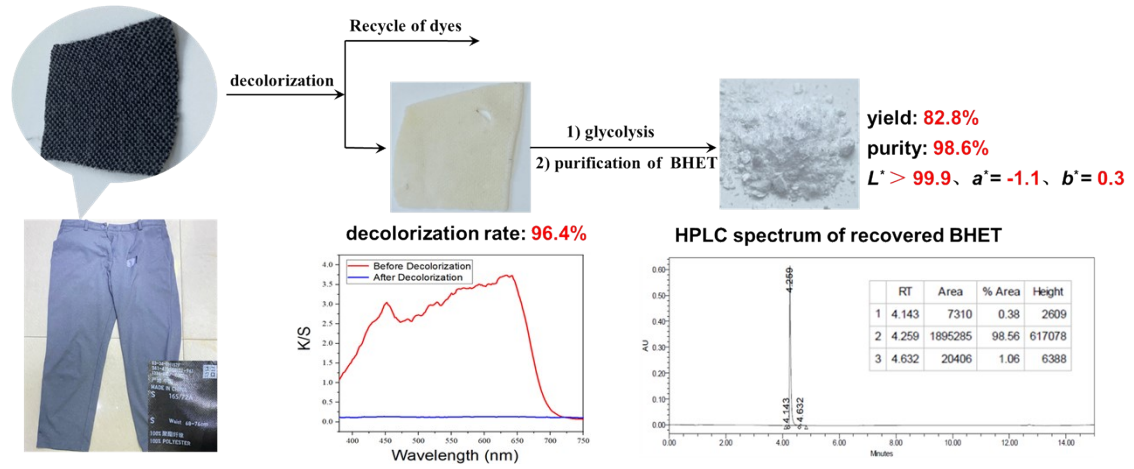


Chromaticity of recovered BHET:

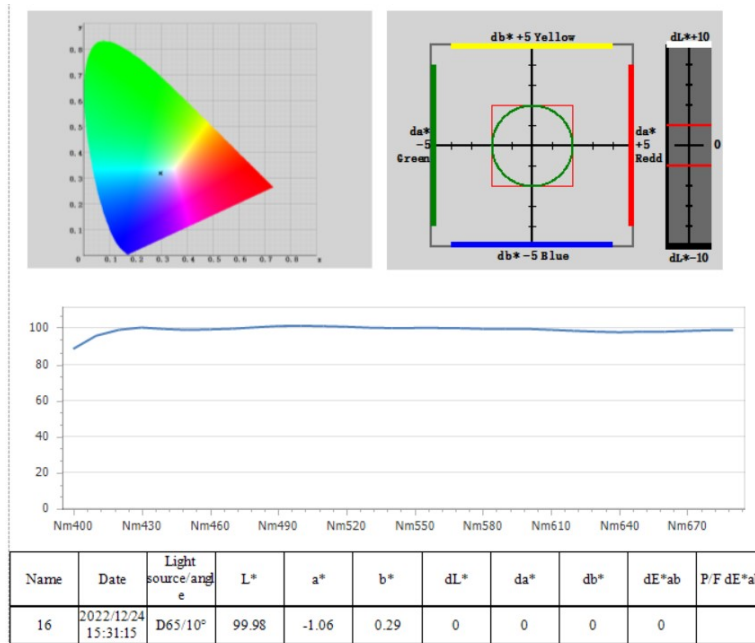


3.16 Sample 16

Composition: 100% Polyester

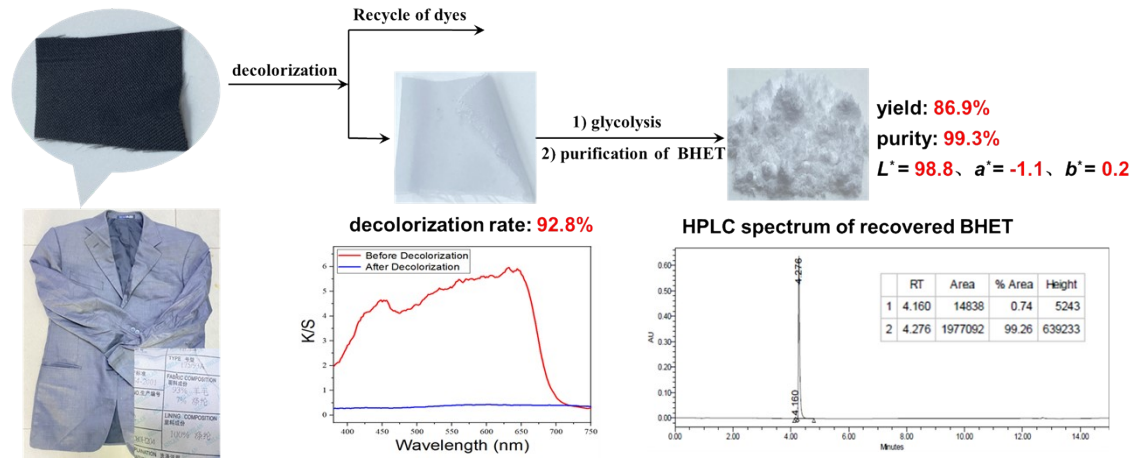


Chromaticity of recovered BHET:

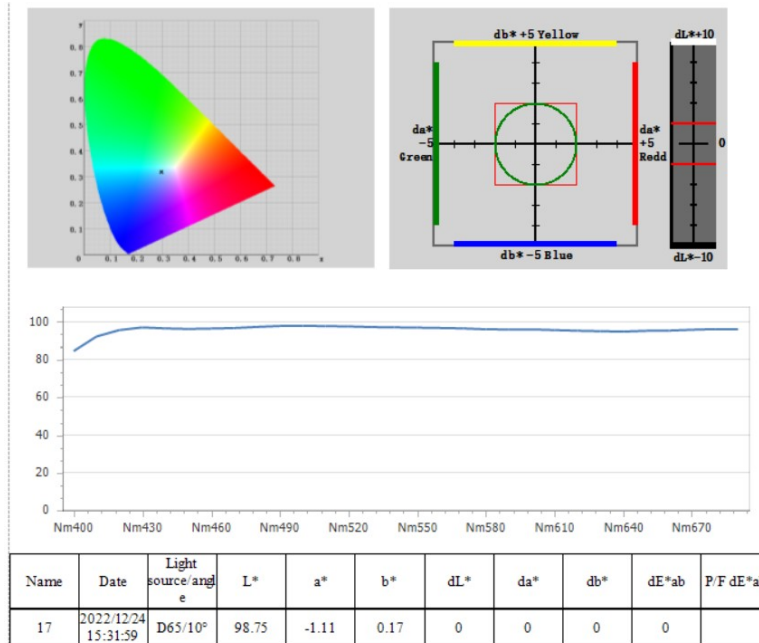


3.17 Sample 17

Composition: 100% Polyester

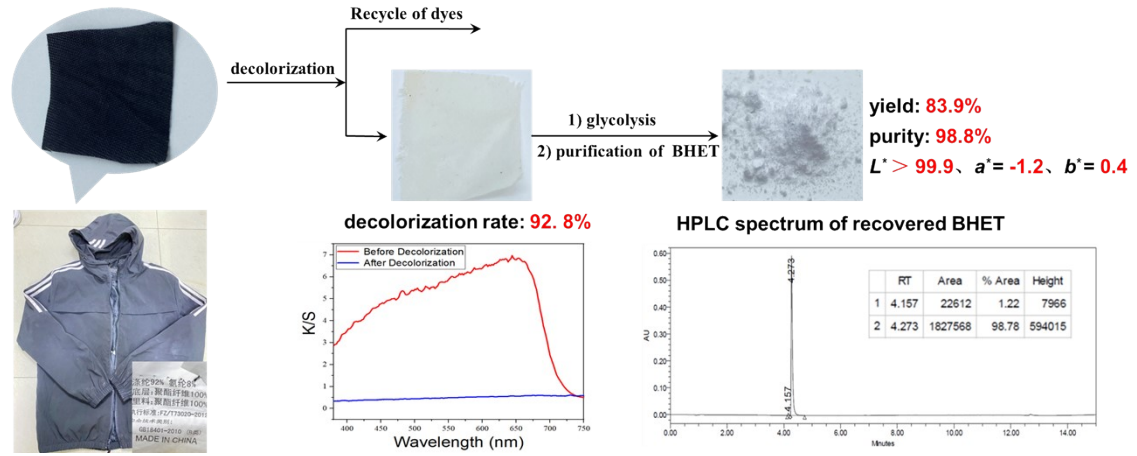


Chromaticity of recovered BHET:

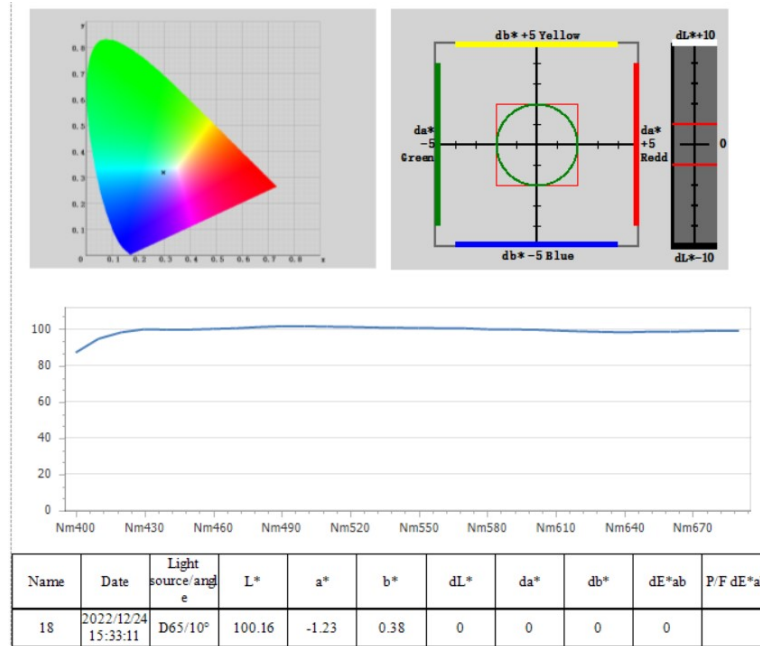


3.18 Sample 18

Composition: 92% Polyester、8% Spandex

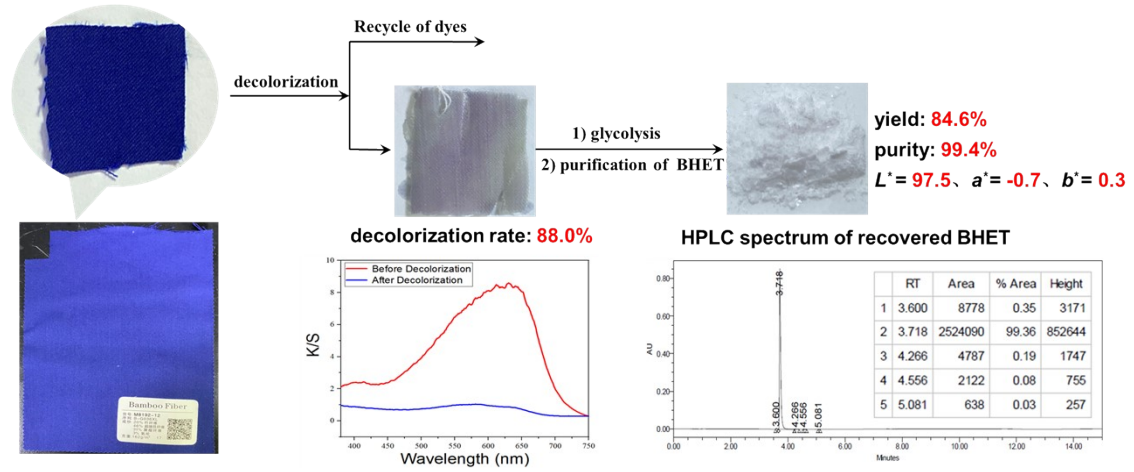


Chromaticity of recovered BHET:

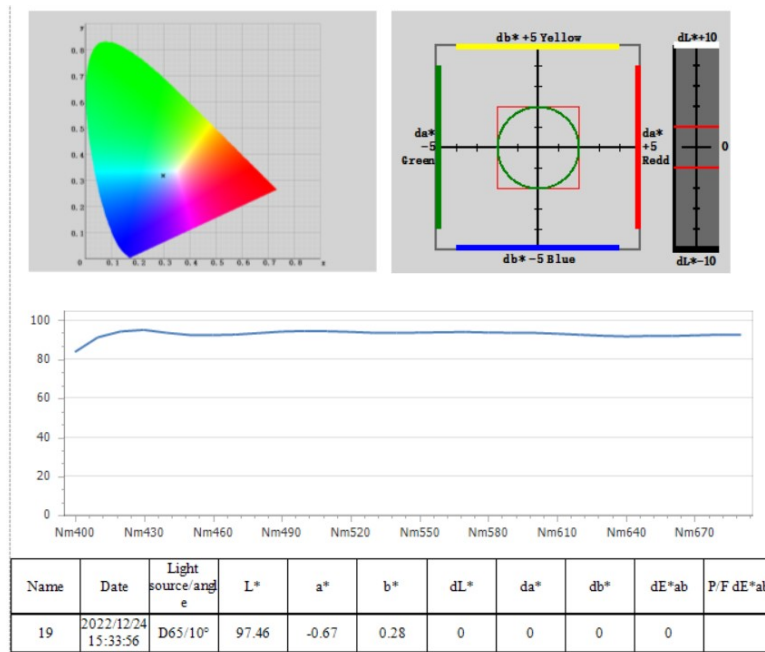


3.19 Sample 19

Composition: 31% Polyester, 46% Polypropylene, 20% Bamboo Fiber, 3% Spandex

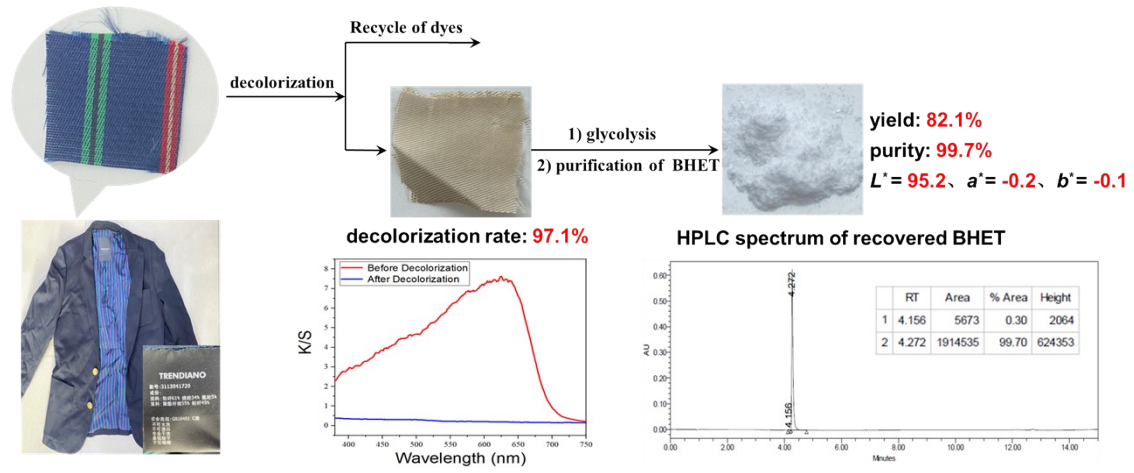


Chromaticity of recovered BHET:

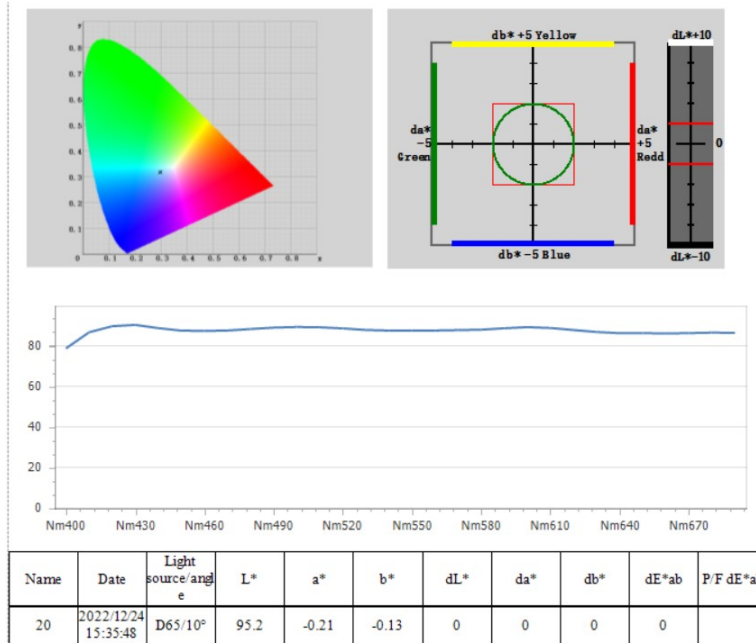


3.20 Sample 20

Composition: 55% Polyester, 45% Viscose

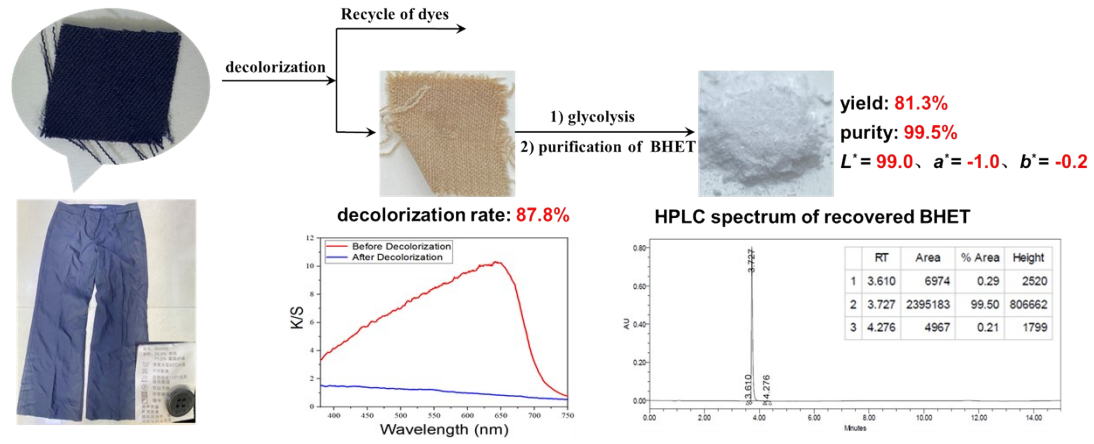


Chromaticity of recovered BHET:

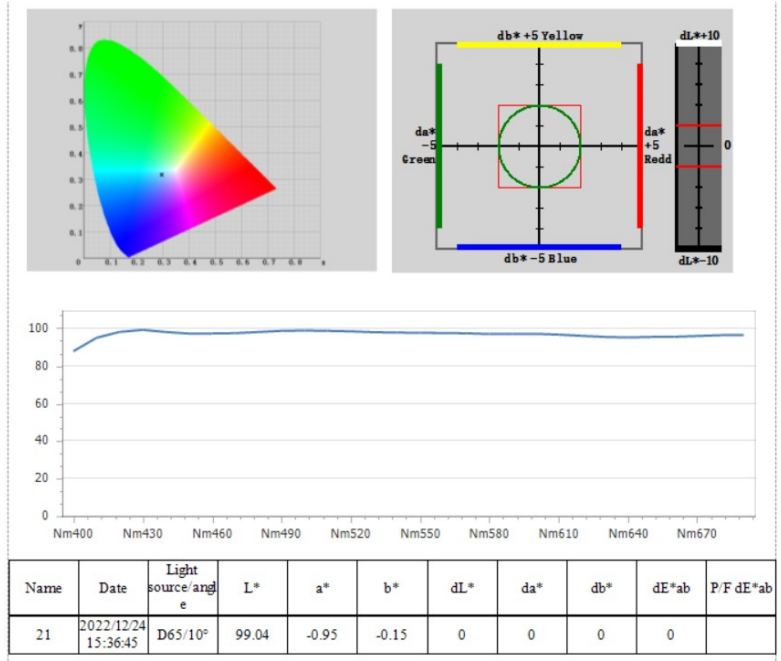


3.21 Sample 21

Composition: 71.2% Polyester, 28.8% Wool

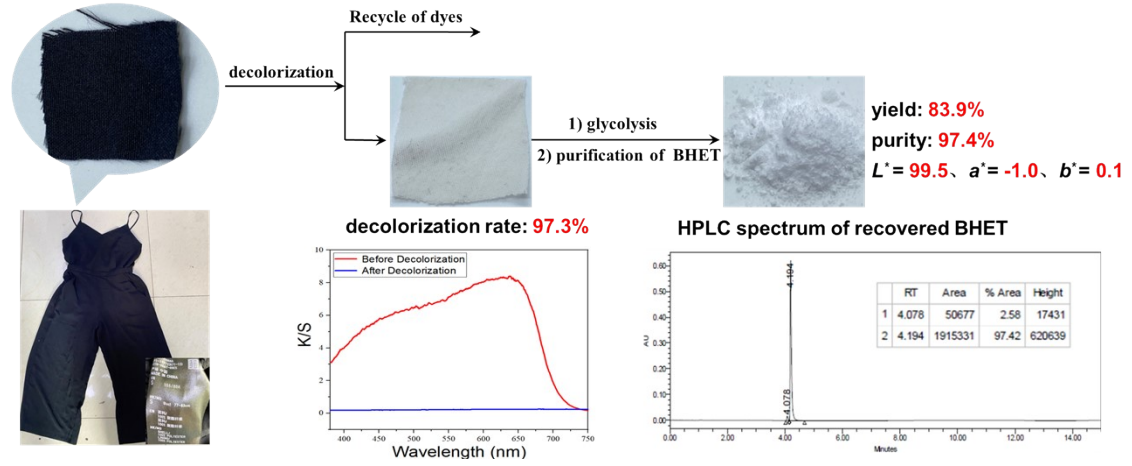


Chromaticity of recovered BHET:

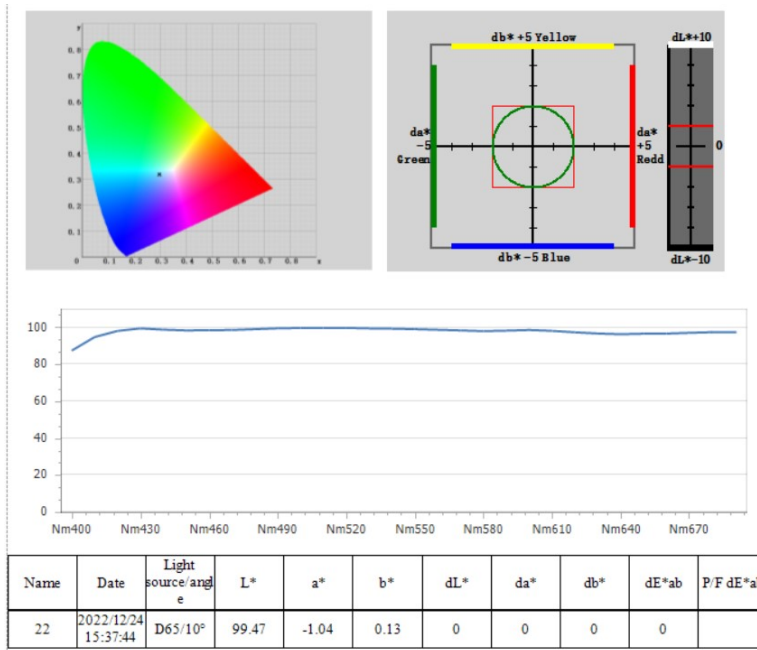


3.22 Sample 22

Composition: 100% Polyester

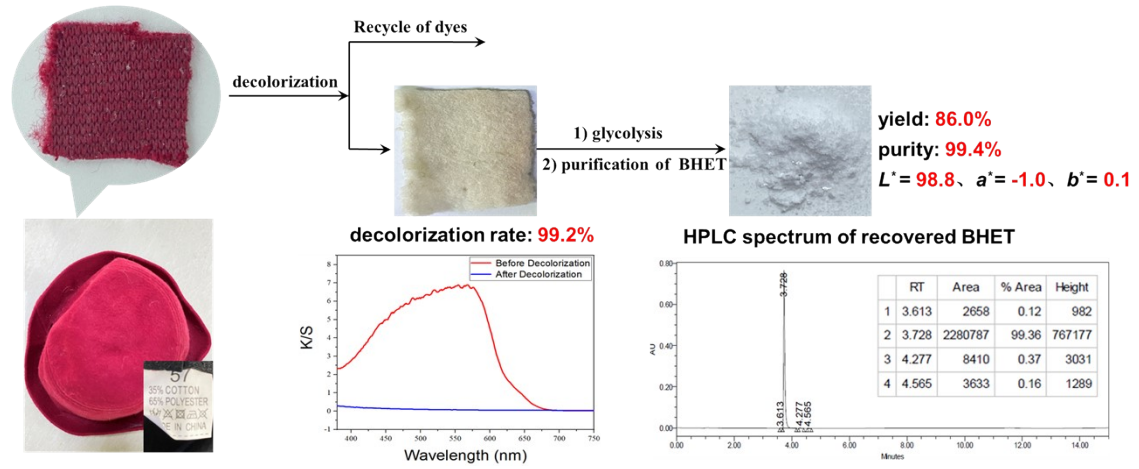


Chromaticity of recovered BHET:

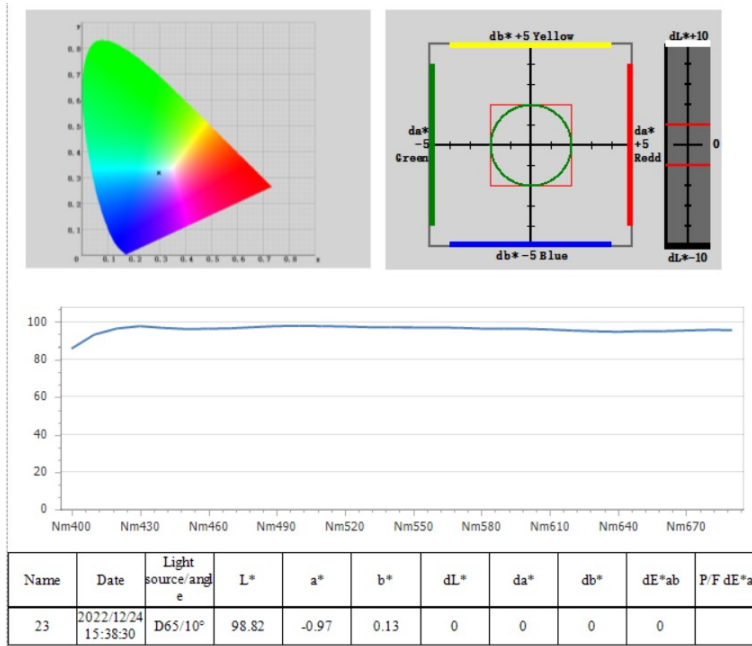


3.23 Sample 23

Composition: 65% Polyester, 35% Cotton

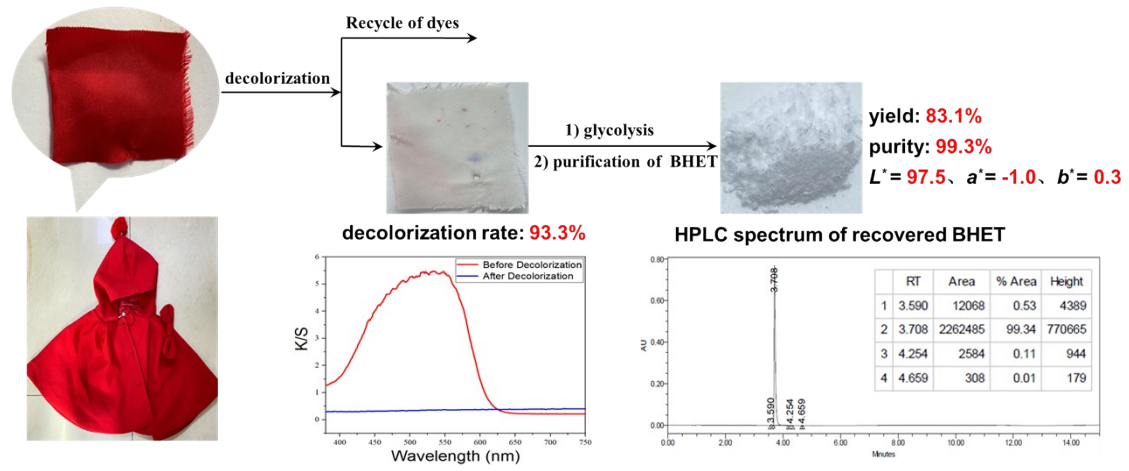


Chromaticity of recovered BHET:

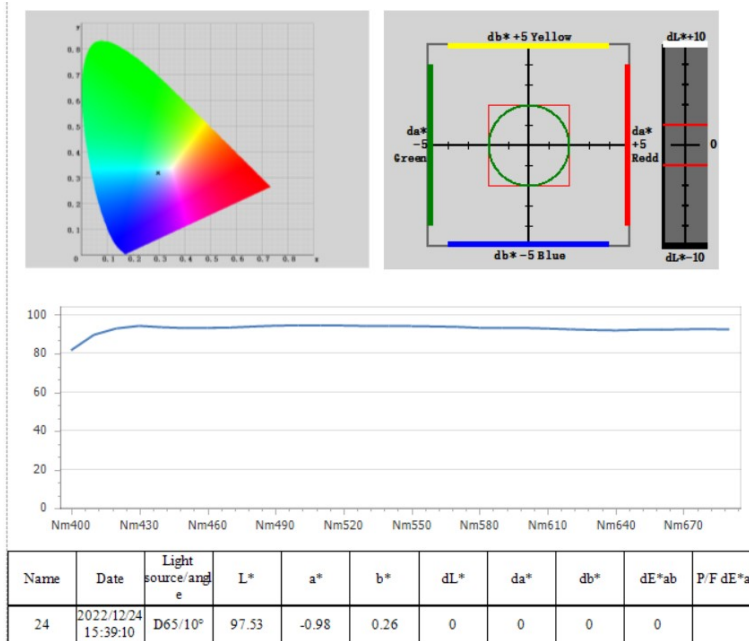


3.24 Sample 24

Composition : 100% Polyester

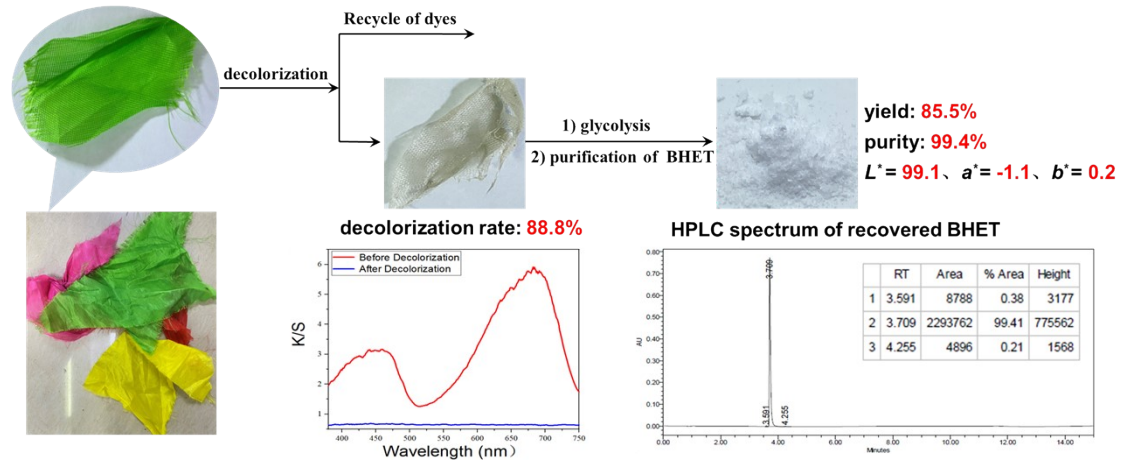


Chromaticity of recovered BHET:

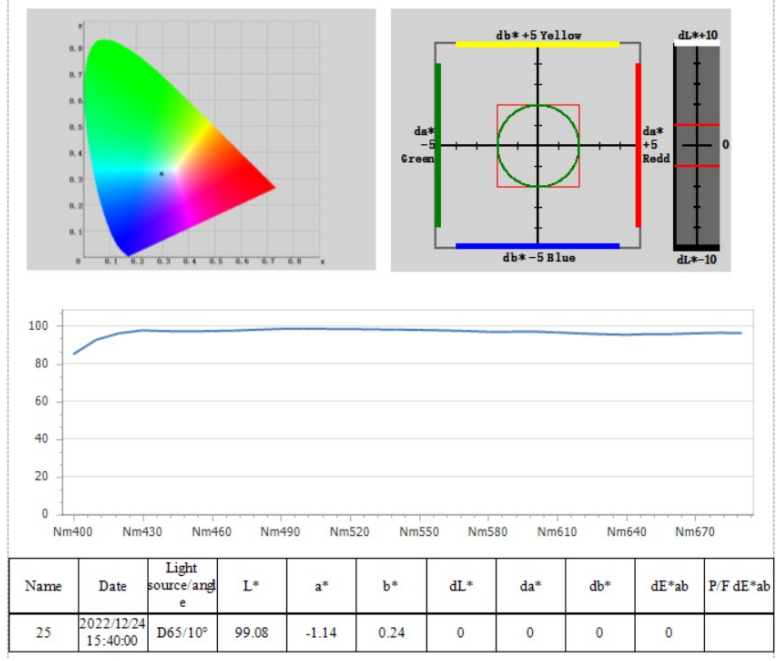


3.25 Sample 25

Composition: 100% Polyester

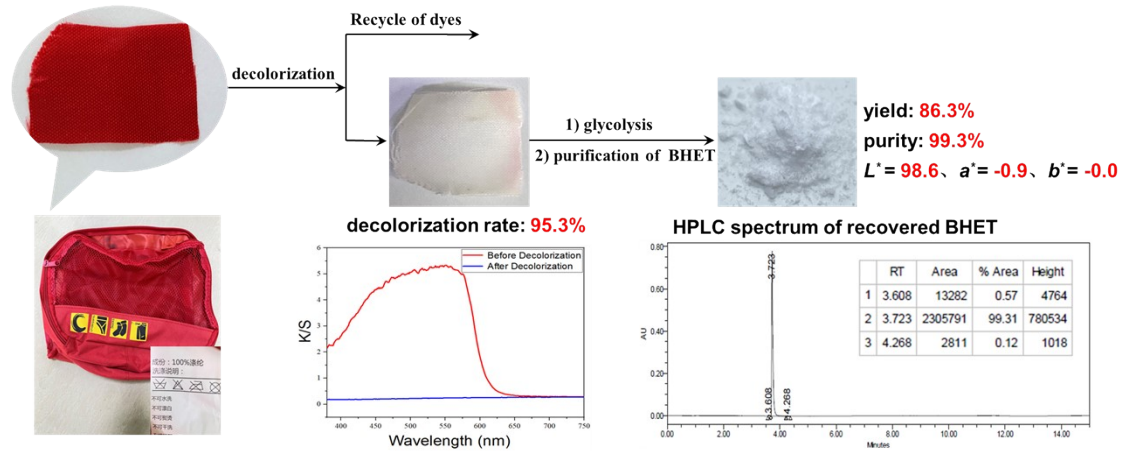


Chromaticity of recovered BHET:

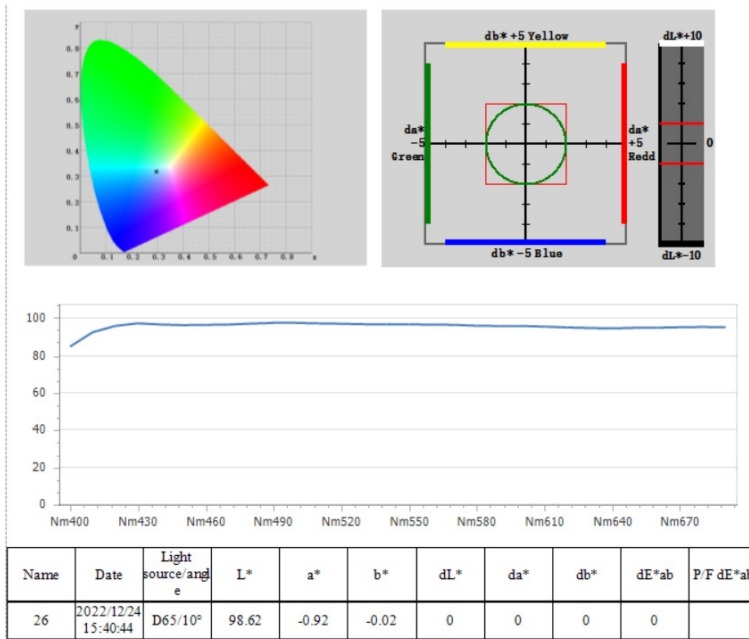


3.26 Sample 26

Composition: 100% Polyester

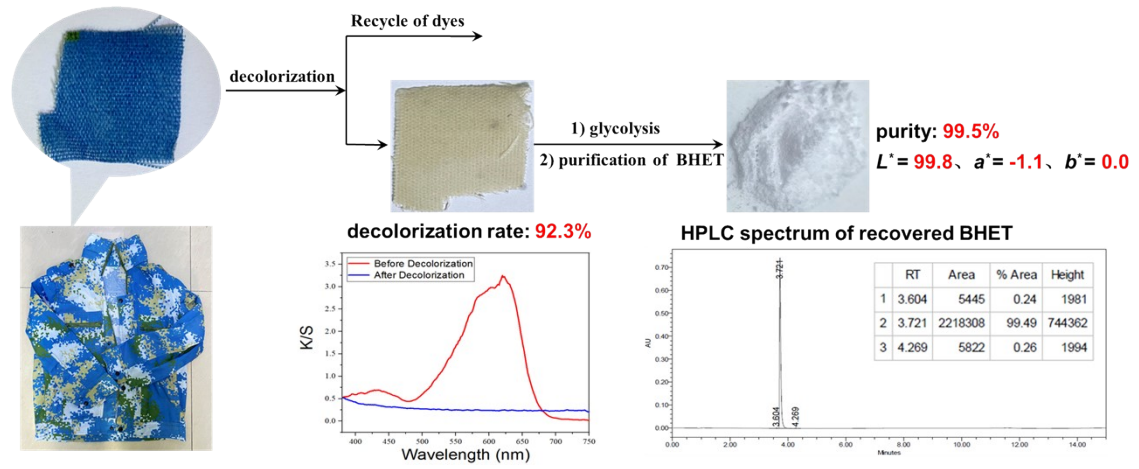


Chromaticity of recovered BHET:

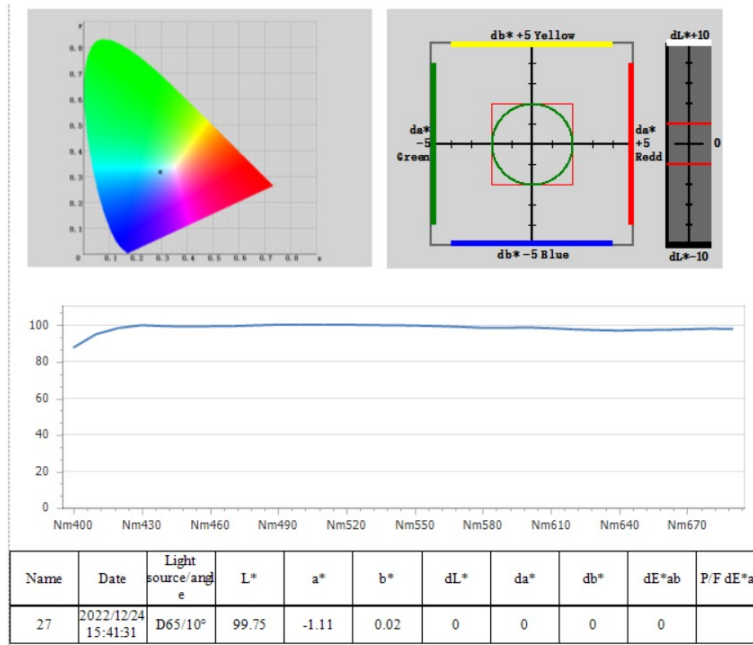


3.27 Sample 27

Composition: Unknown

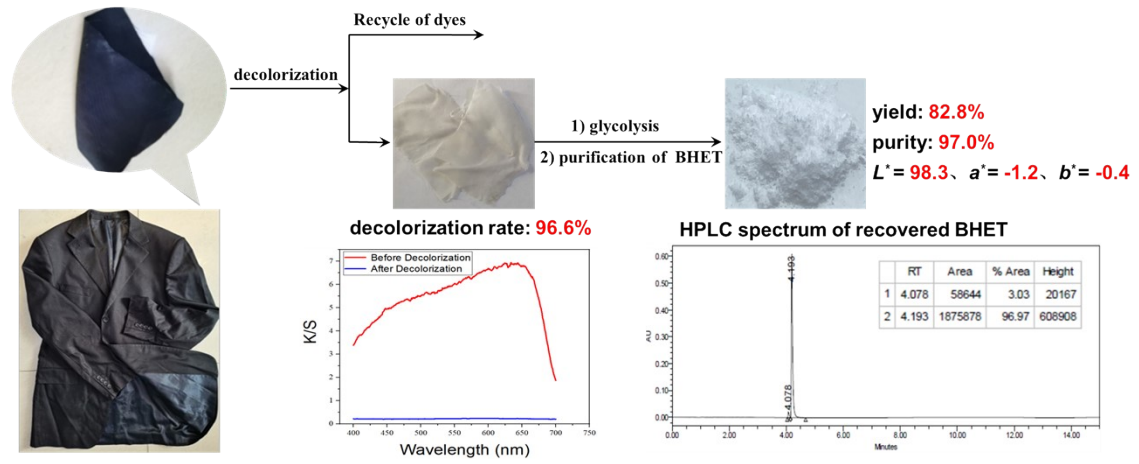


Chromaticity of recovered BHET:

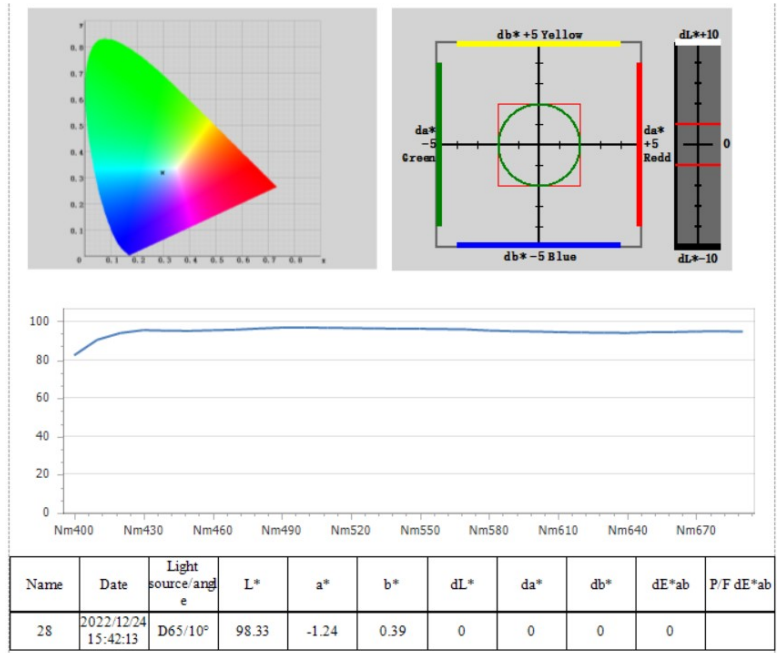


3.28 Sample 28

Composition: 100% Polyester

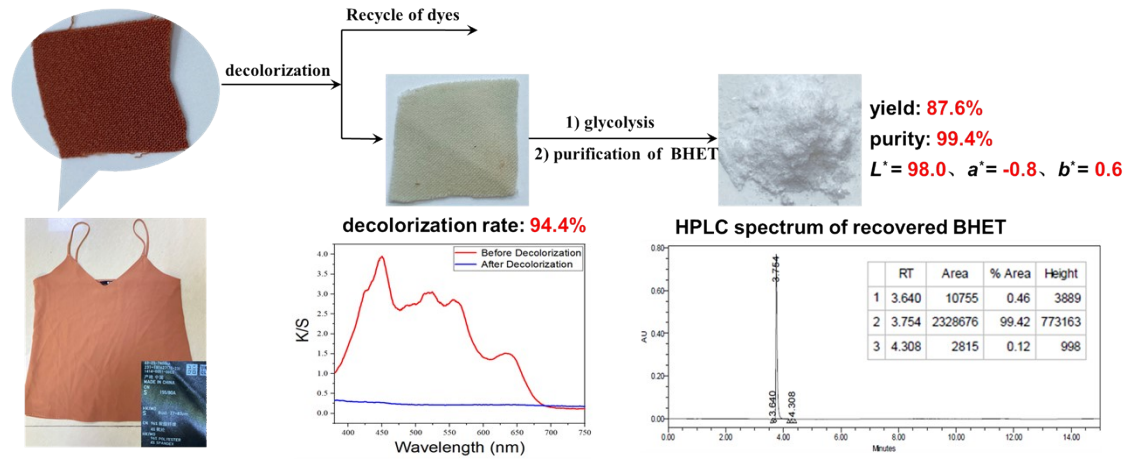


Chromaticity of recovered BHET:

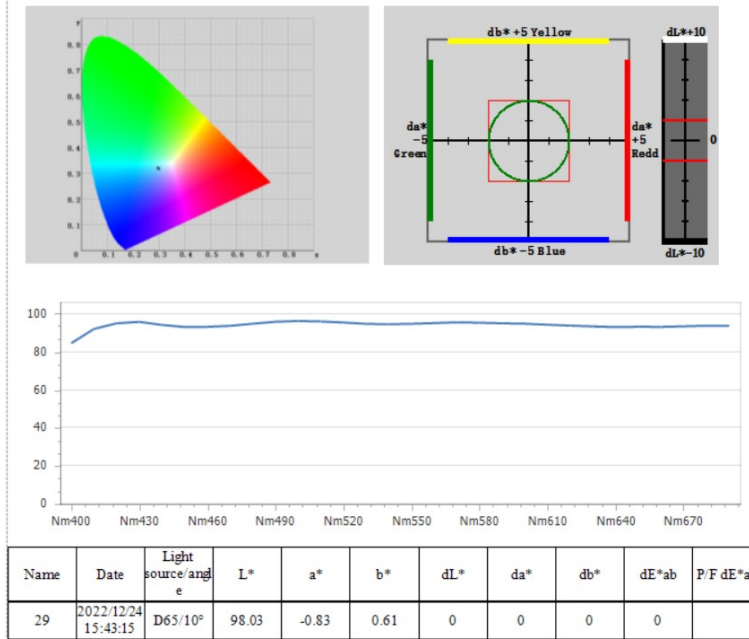


3.29 Sample 29

Composition: 96% Polyester, 4% Spandex

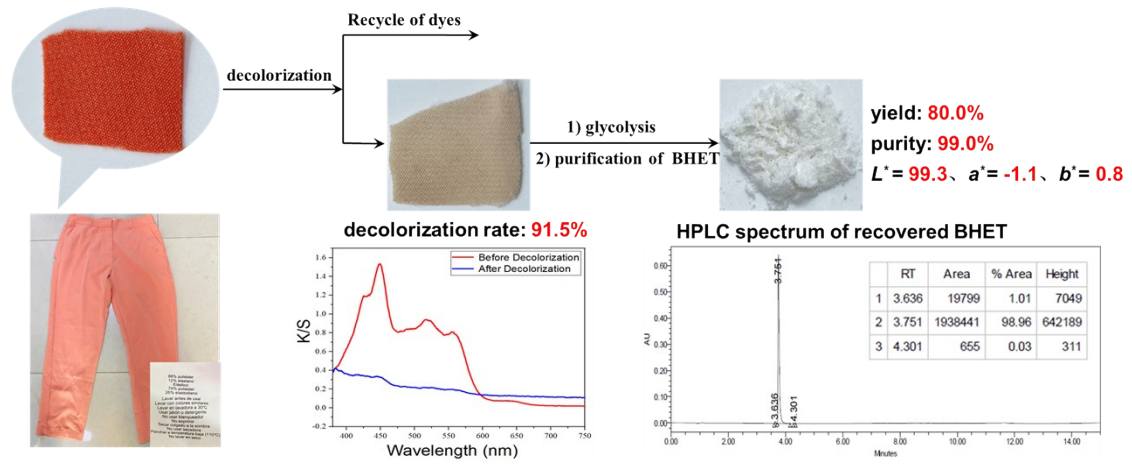


Chromaticity of recovered BHET:

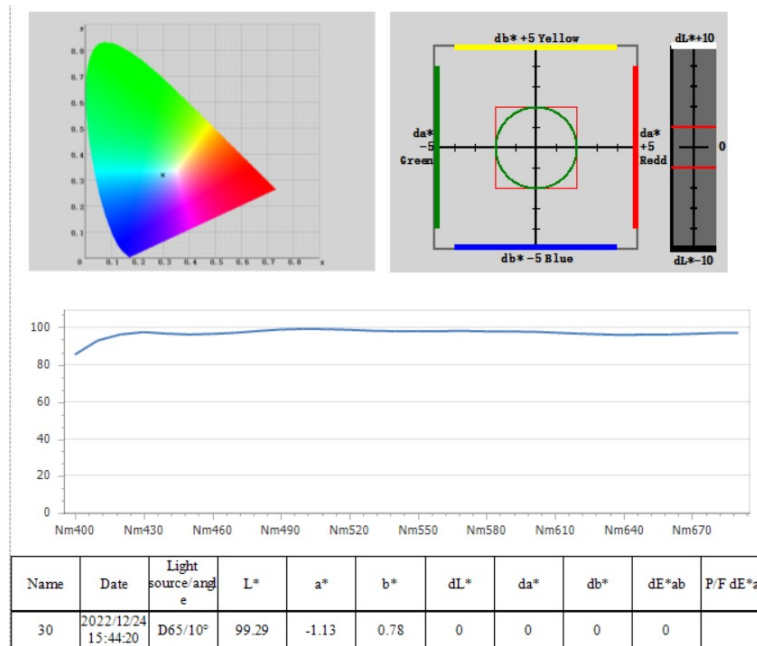


3.30 Sample 30

Composition: 88% Polyester, 12% Spandex

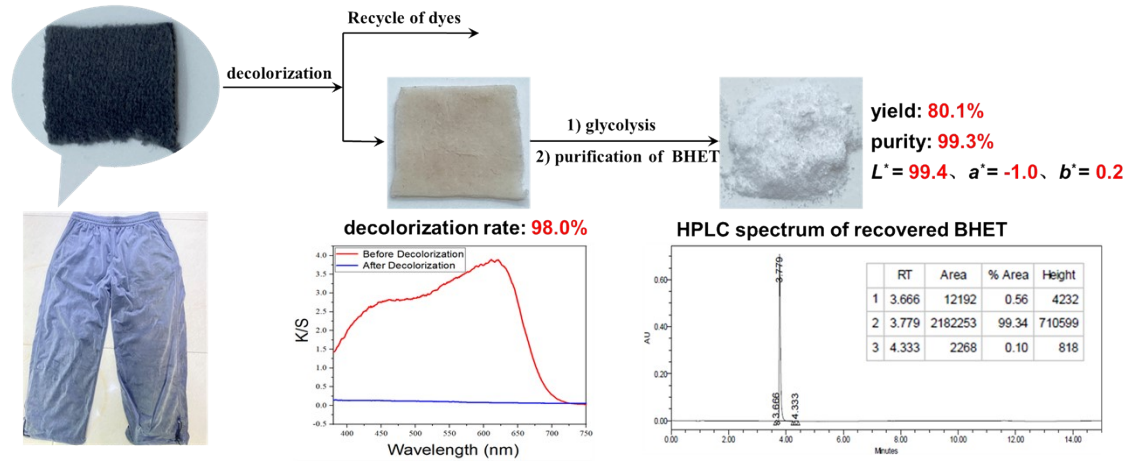


Chromaticity of recovered BHET:

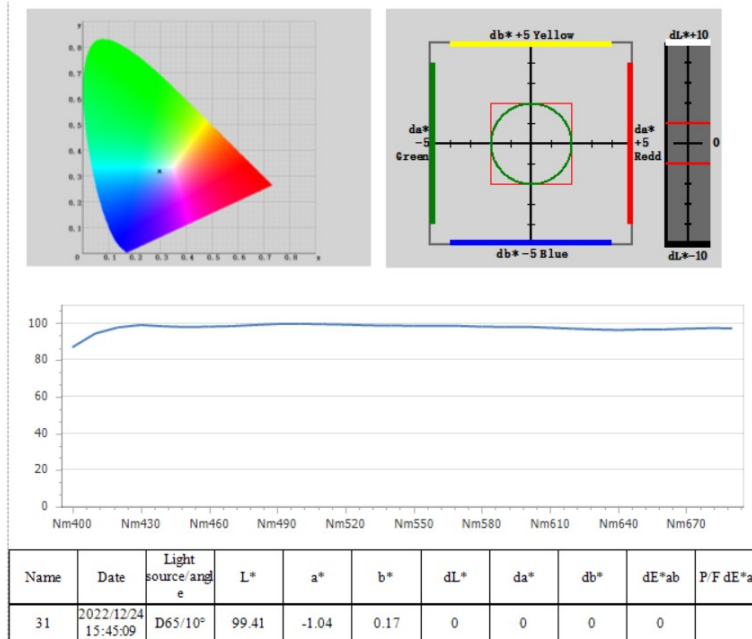


3.31 Sample 31

Composition: 100% Polyester

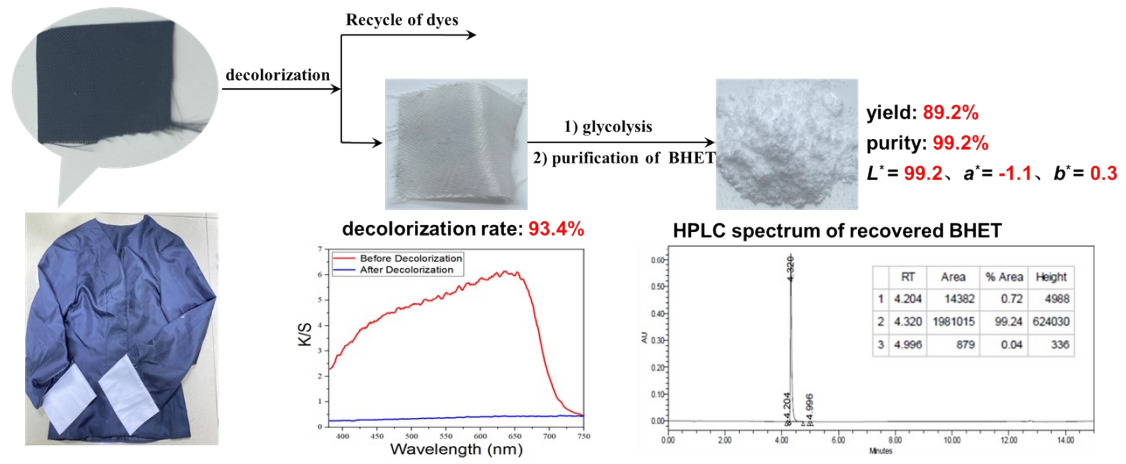


Chromaticity of recovered BHET:

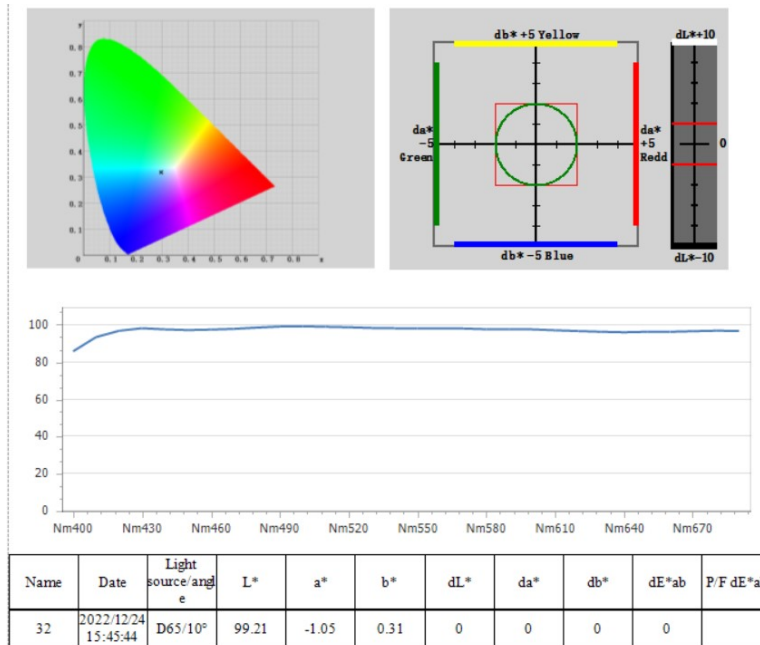


3.32 Sample 32

Composition: 100% Polyester

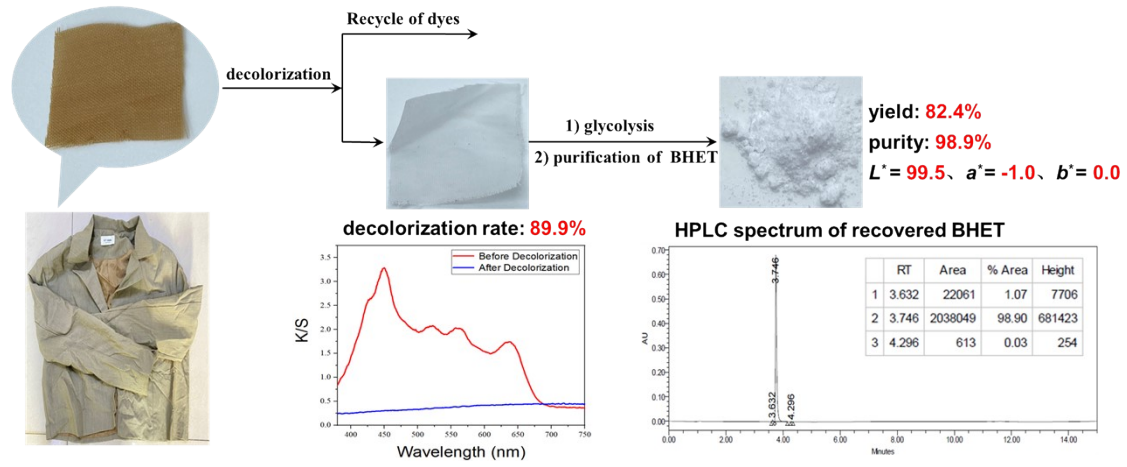


Chromaticity of recovered BHET:

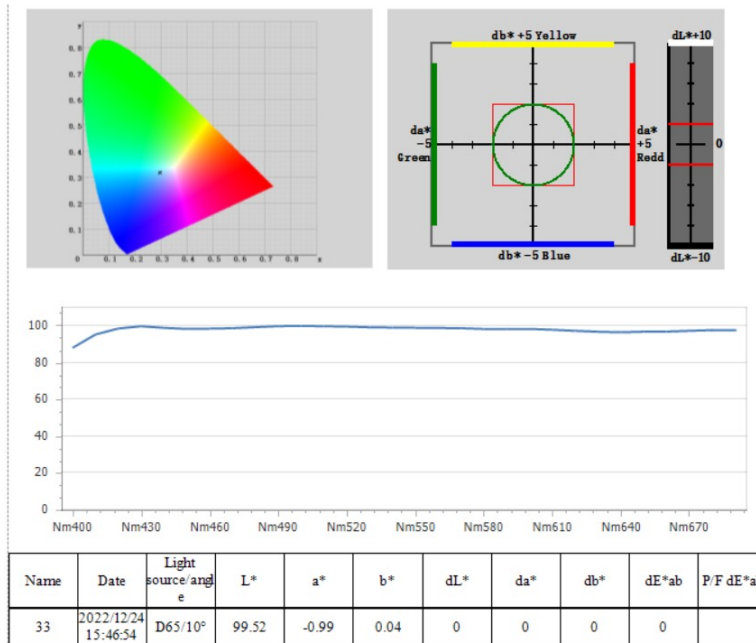


3.33 Sample 33

Composition: 100% Polyester

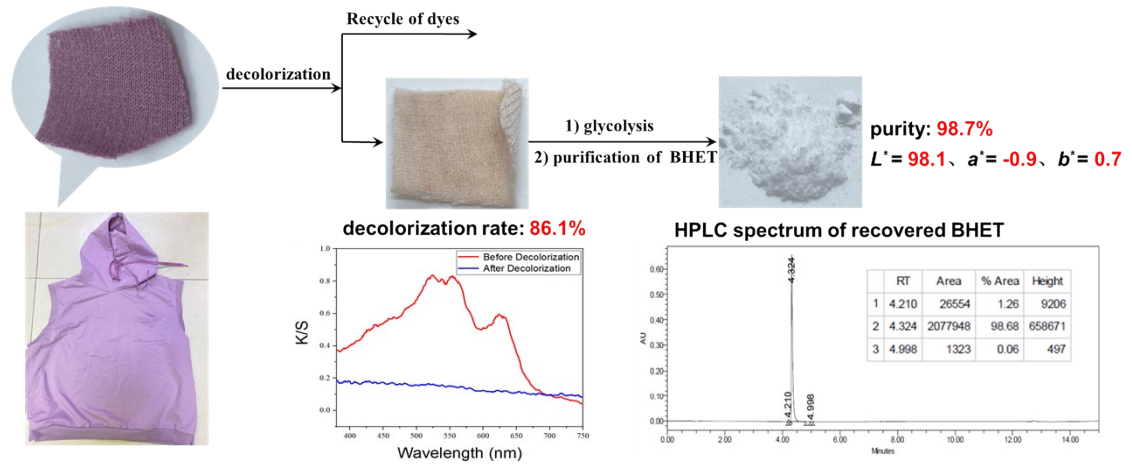


Chromaticity of recovered BHET:

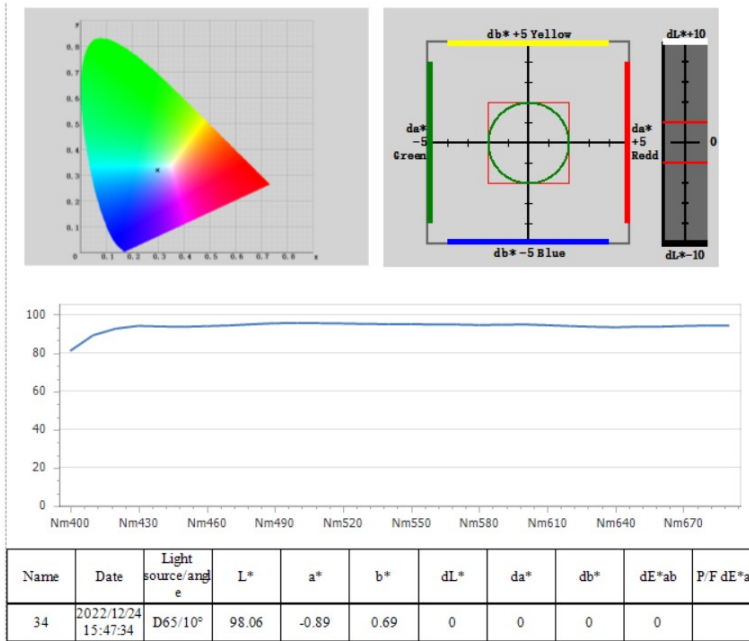


3.34 Sample 34

Composition: Unknown

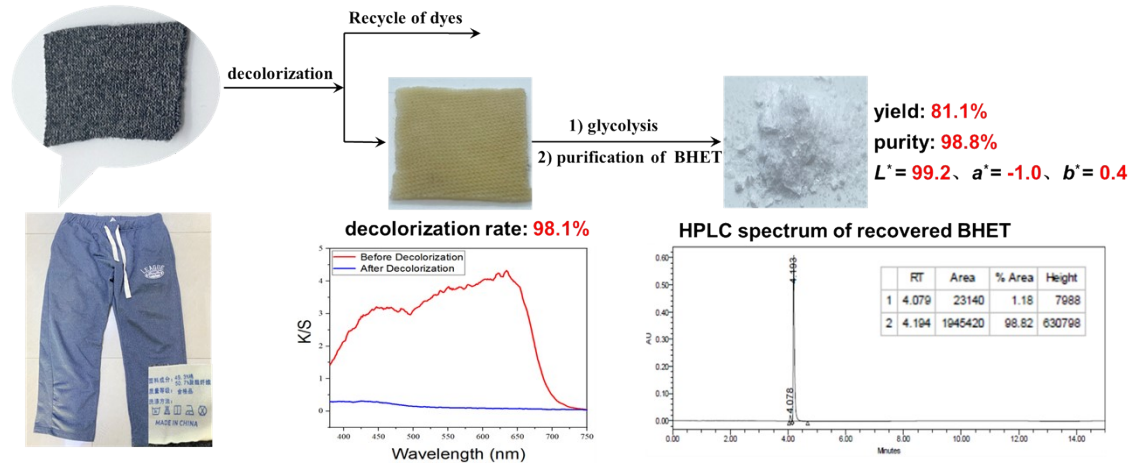


Chromaticity of recovered BHET:

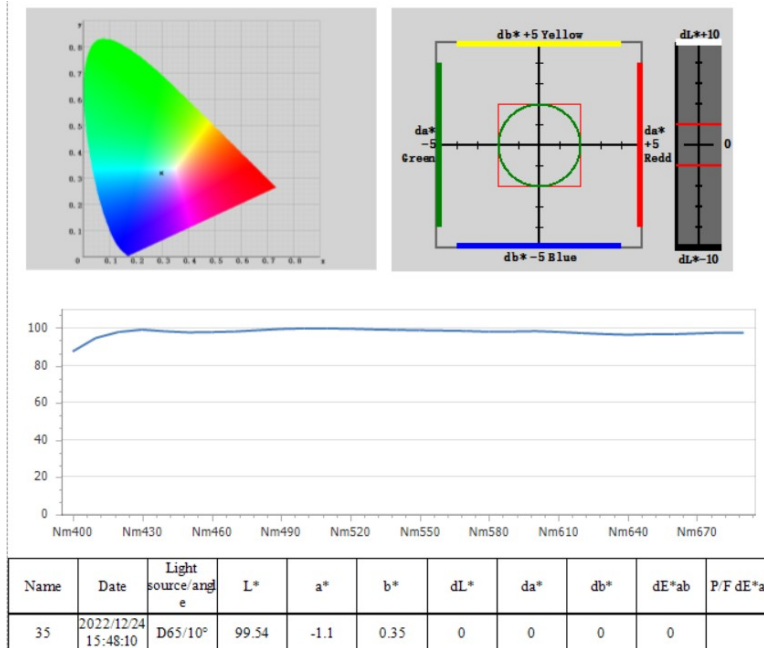


3.35 Sample 35

Composition: 50.7% Polyester、49.3% Cotton

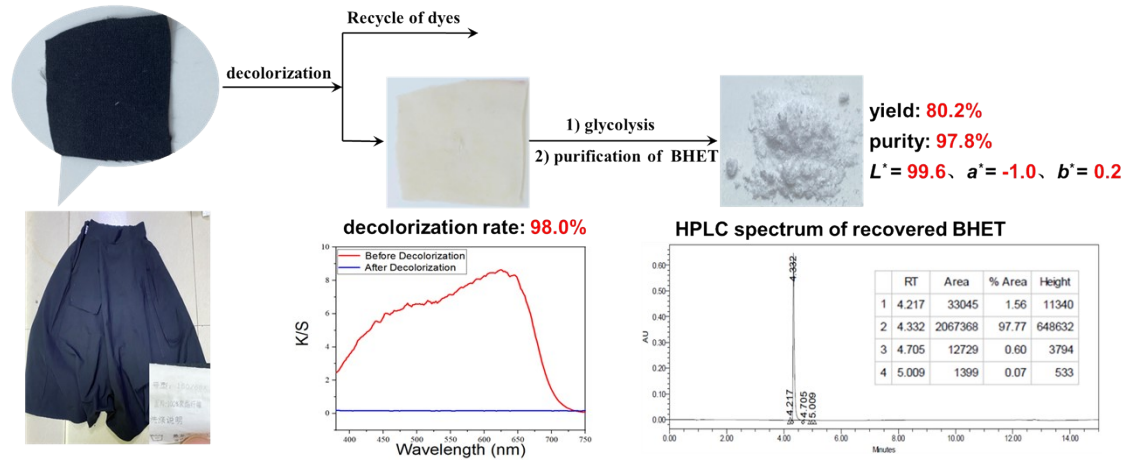


Chromaticity of recovered BHET:

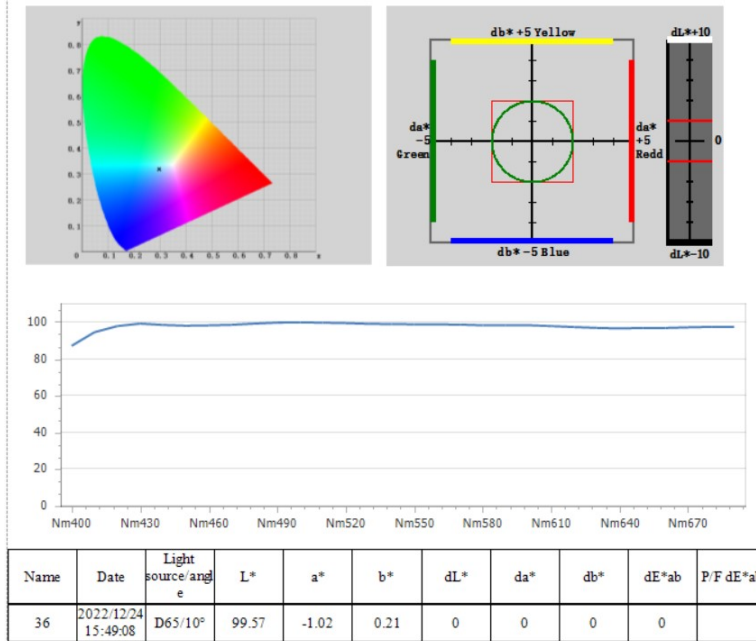


3.36 Sample 36

Composition: 100% Polyester

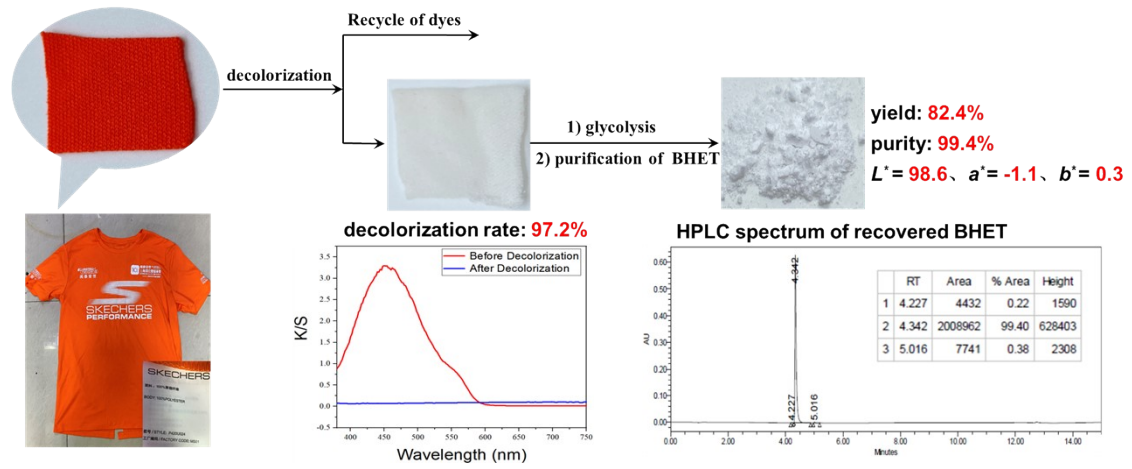


Chromaticity of recovered BHET:

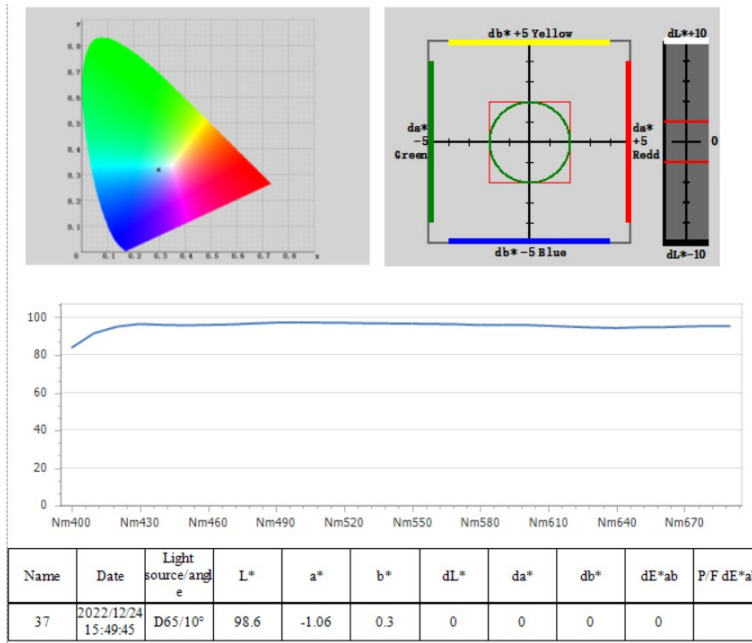


3.37 Sample 37

Composition: 100% Polyester

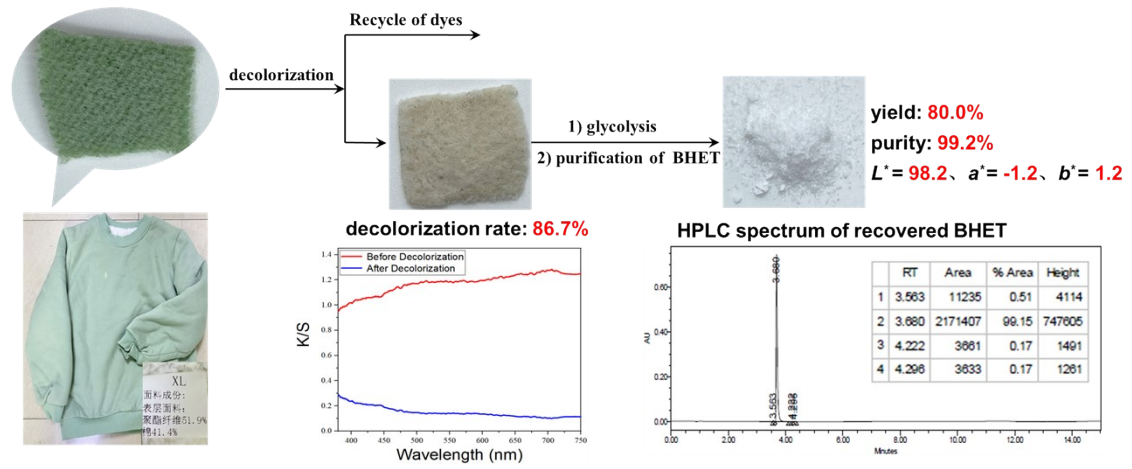


Chromaticity of recovered BHET:

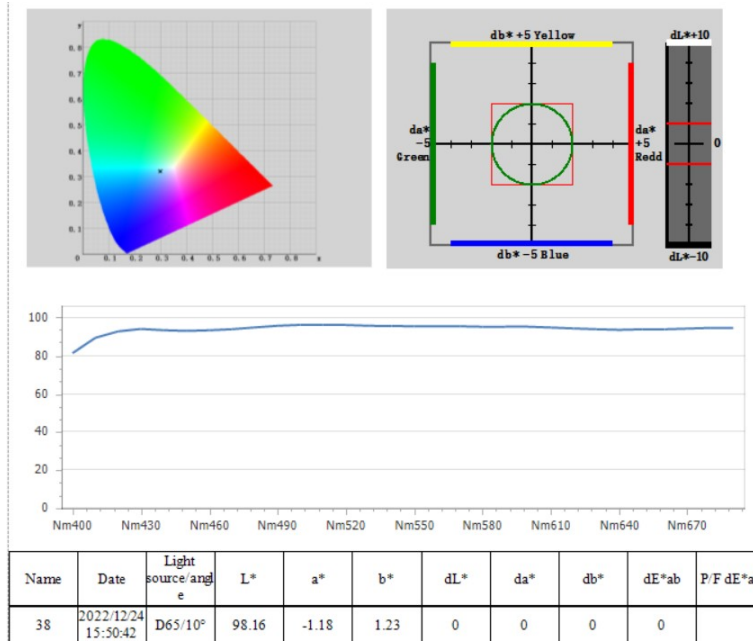


3.38 Sample 38

Composition: 51.9% Polyester, 48.1% Cotton

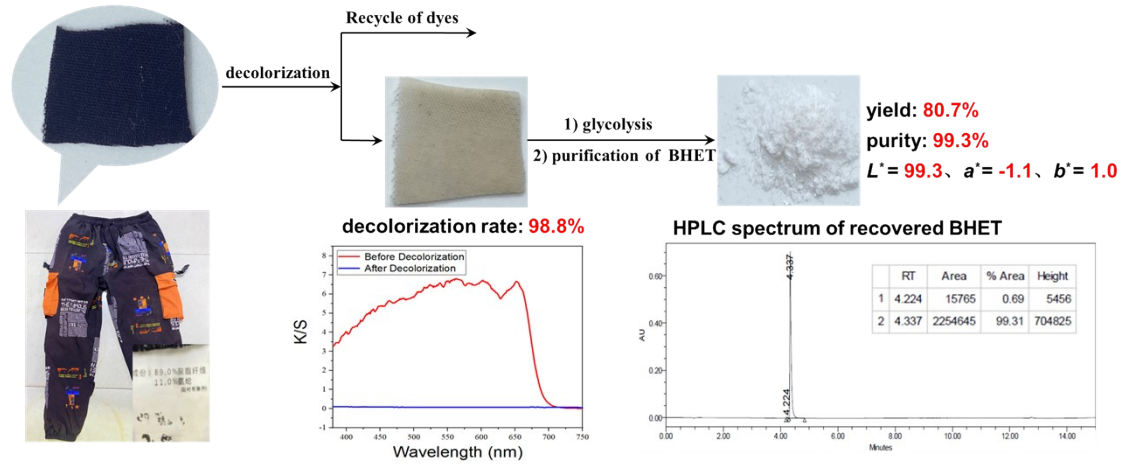


Chromaticity of recovered BHET:

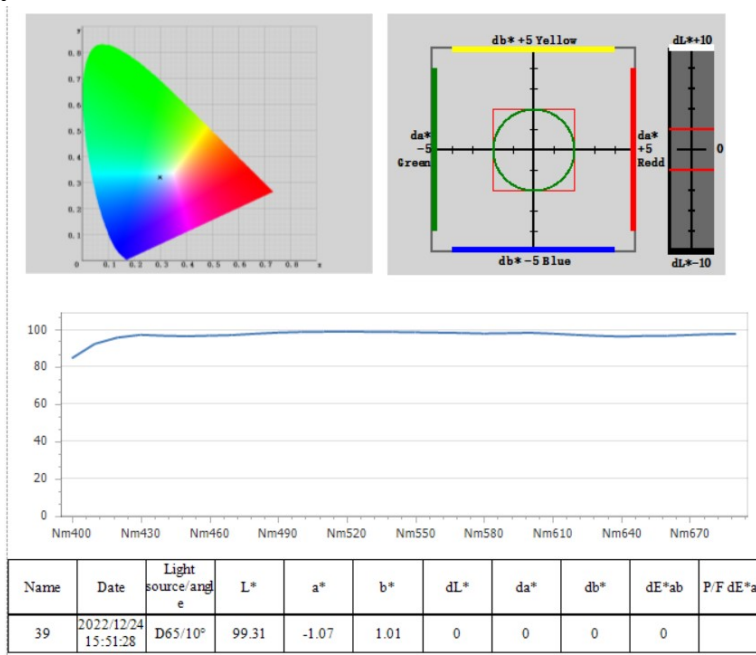


3.39 Sample 39

Composition: 89% Polyester, 11% Spandex

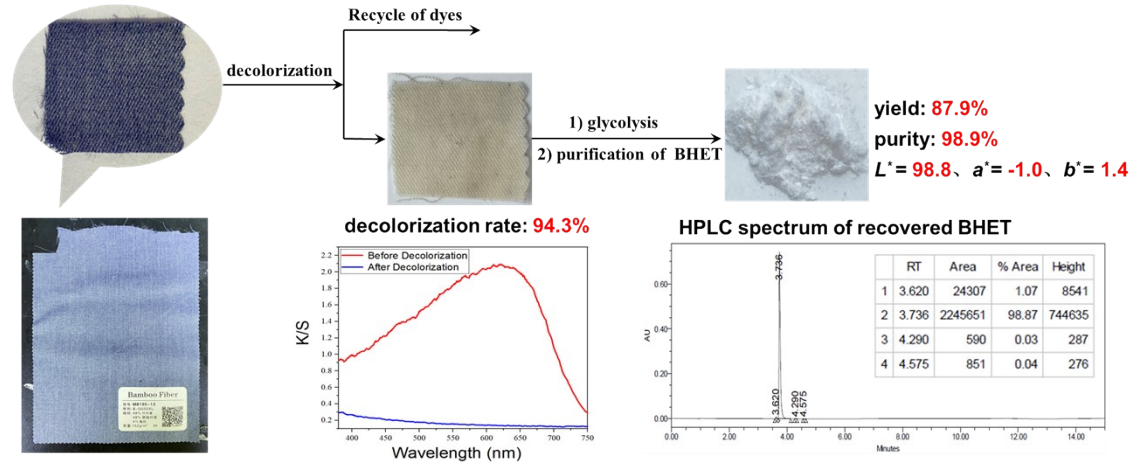


Chromaticity of recovered BHET:

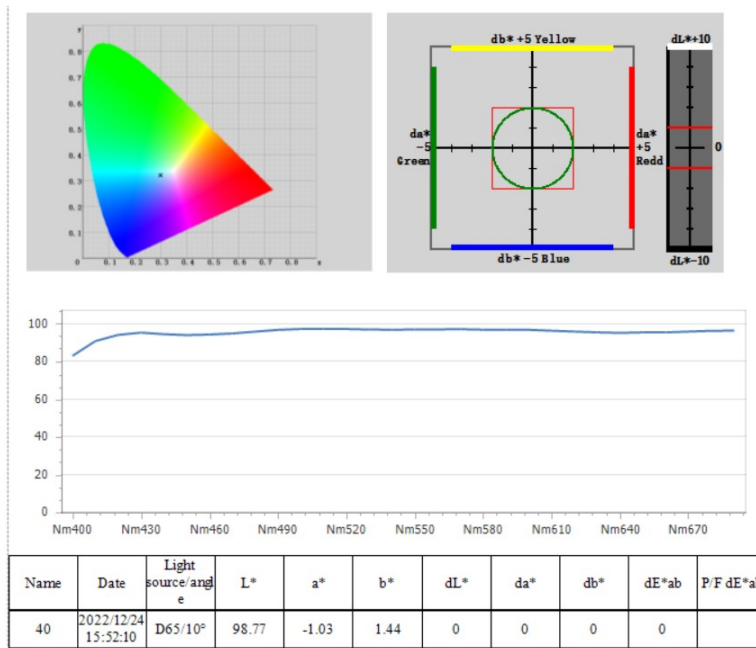


3.40 Sample 40

Composition: 48% Polyester、48% Bamboo Fiber、4%Spandex

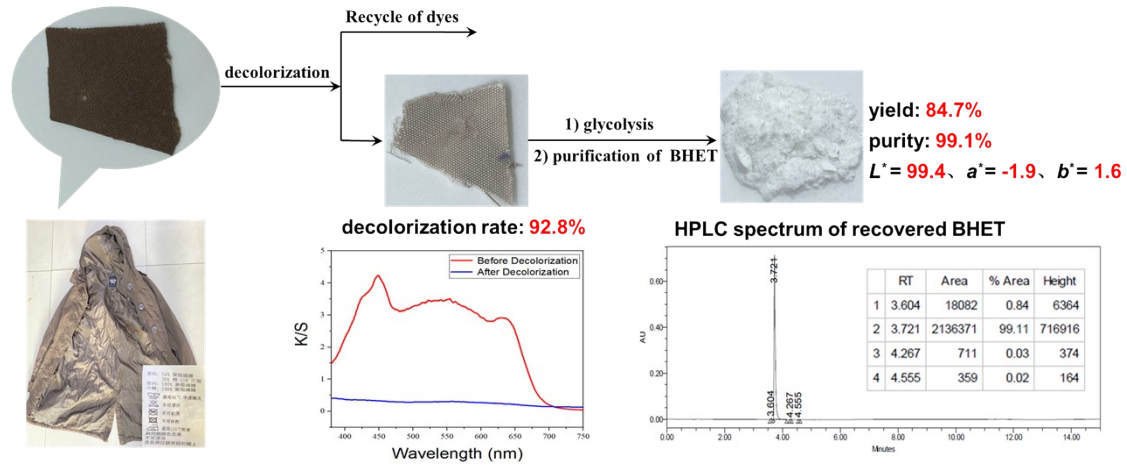


Chromaticity of recovered BHET:

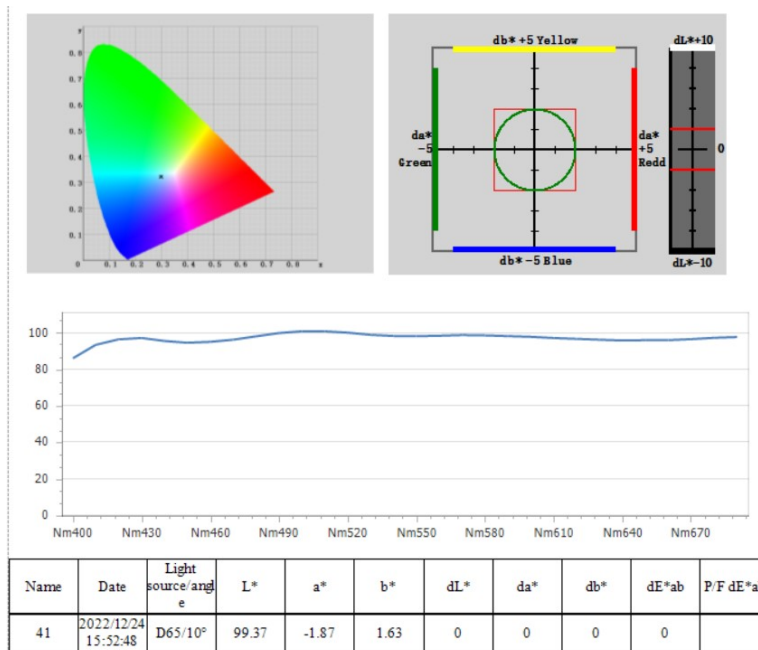


3.41 Sample 41

Composition: 54% Polyester, 35% Cotton, 11% Nylon

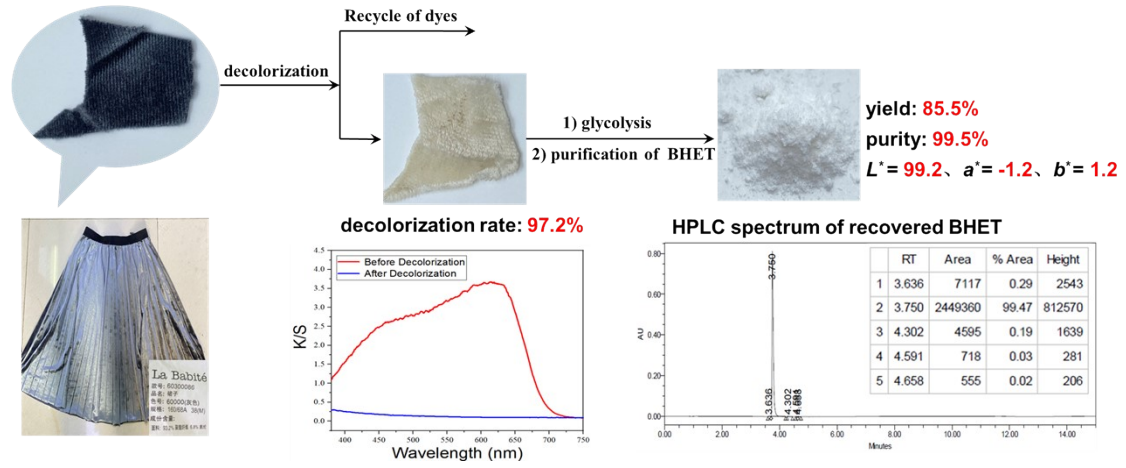


Chromaticity of recovered BHET:

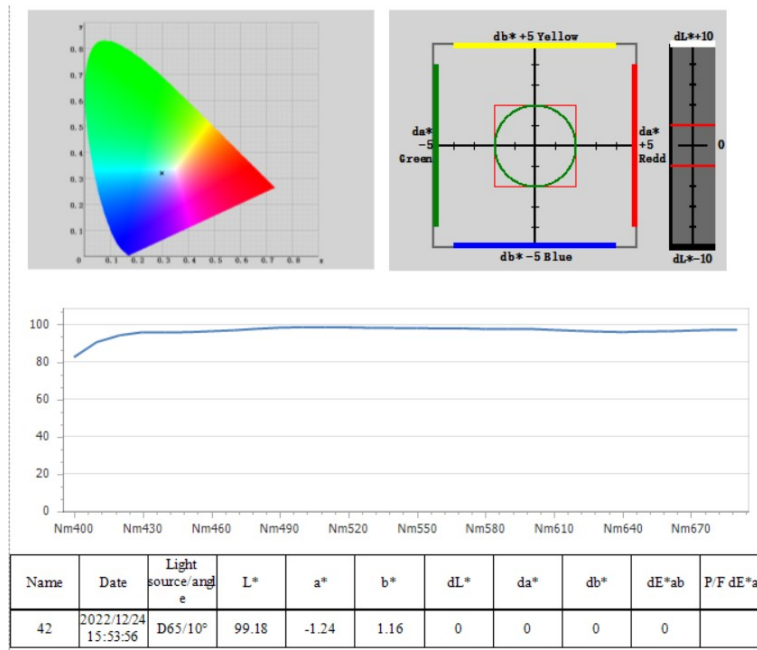


3.42 Sample 42

Composition: 93.2% Polyester, 6.8% Spandex

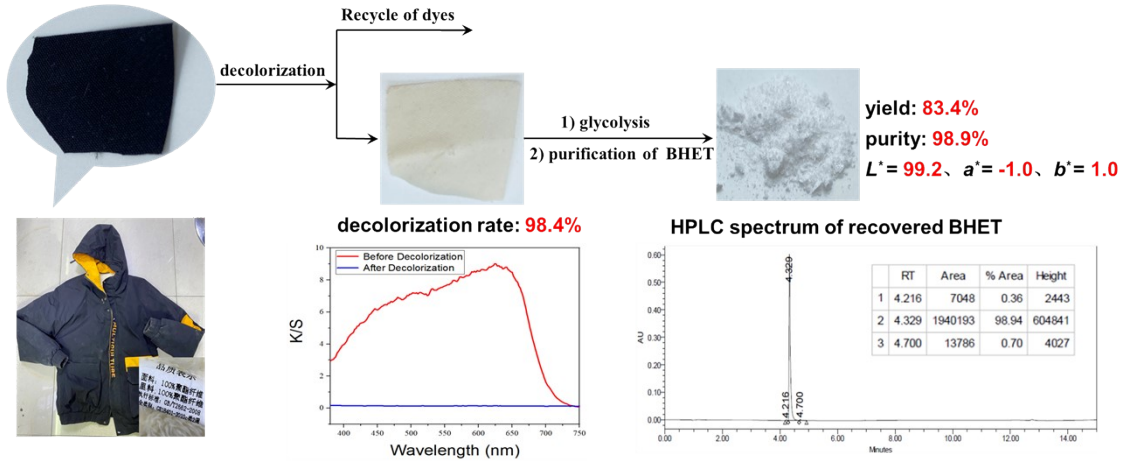


Chromaticity of recovered BHET:

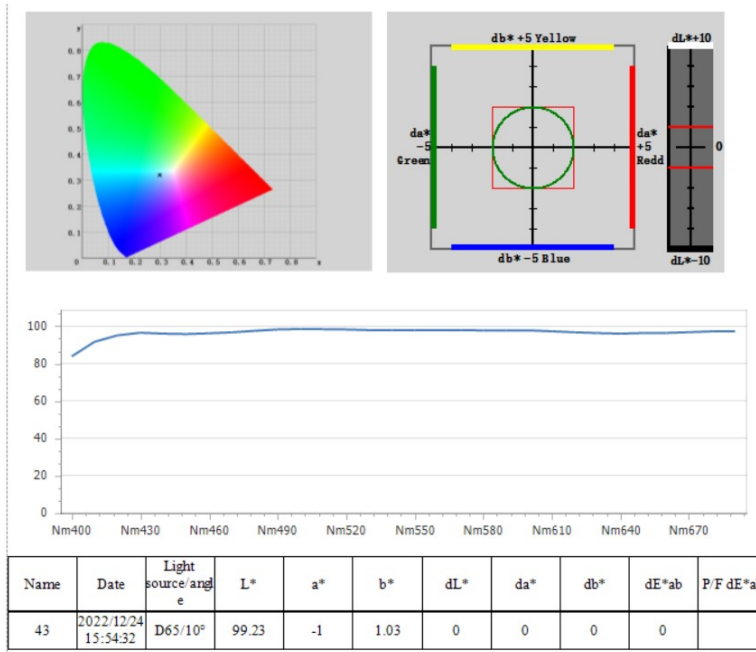


3.43 Sample 43

Composition: 100% Polyester

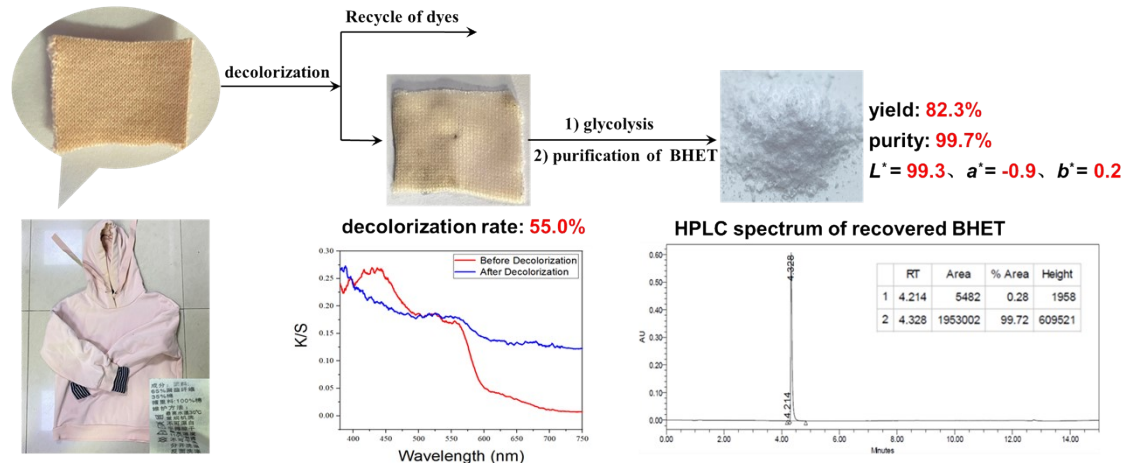


Chromaticity of recovered BHET:

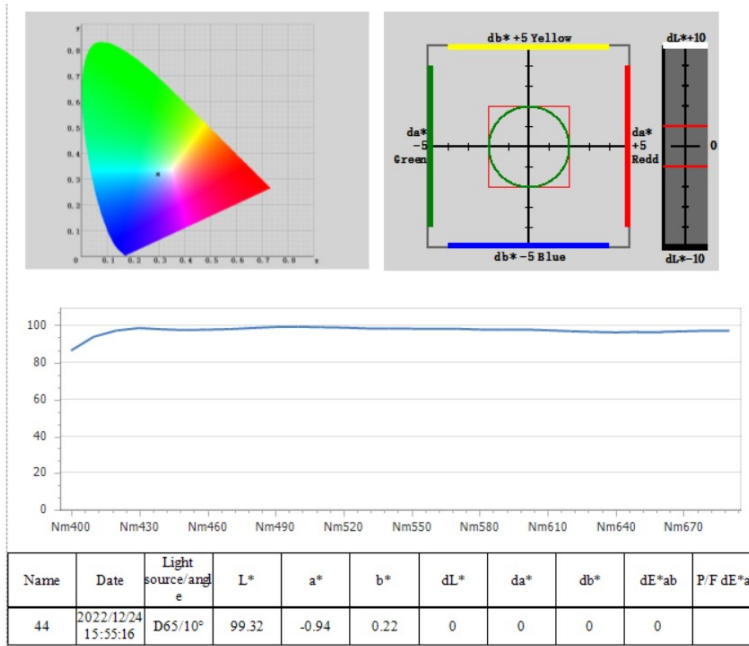


3.44 Sample 44

Composition: 65% Polyester、35% Cotton

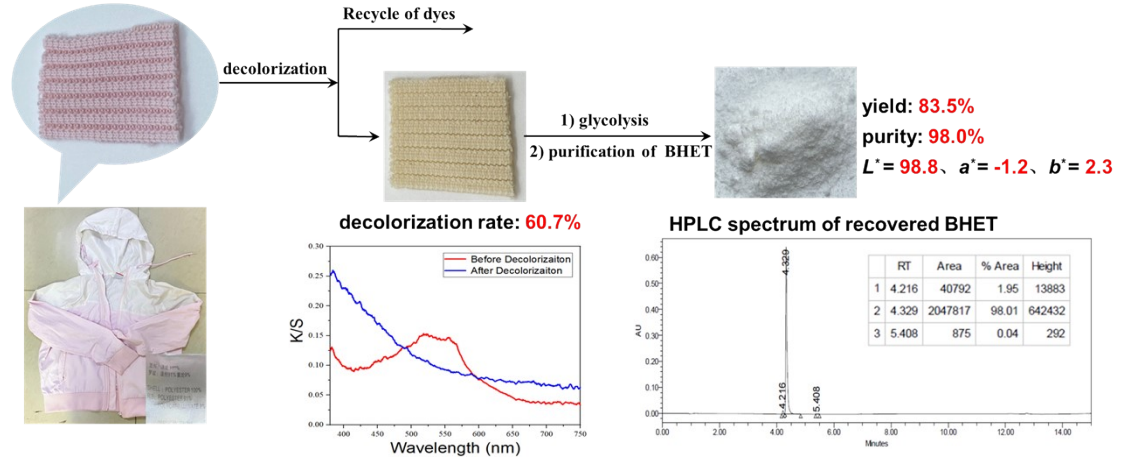


Chromaticity of recovered BHET:

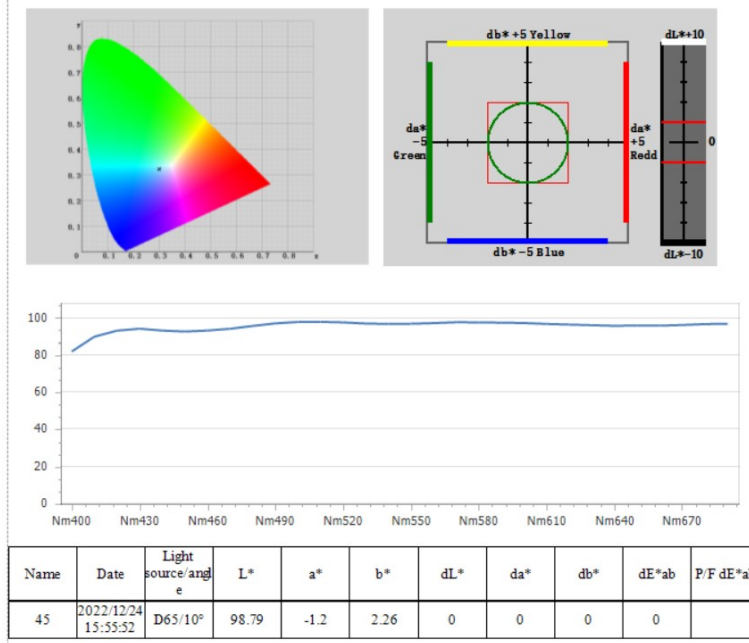


3.45 Sample 45

Composition: 91% Polyester, 9% Spandex

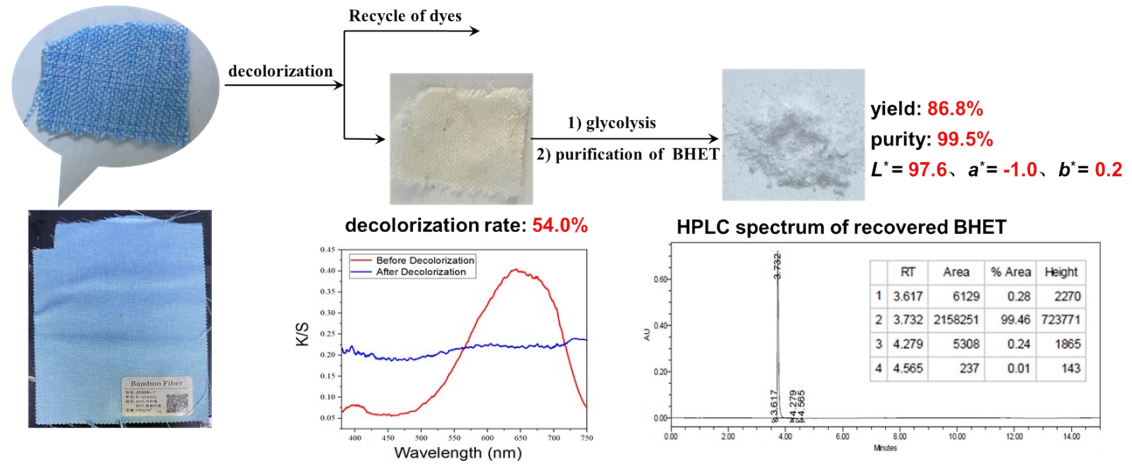


Chromaticity of recovered BHET:

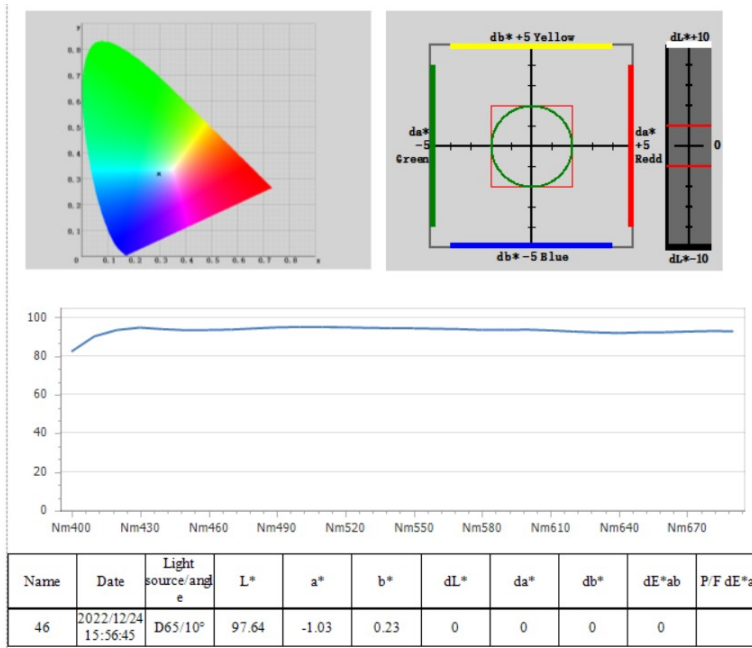


3.46 Sample 46

Composition: 80% Polyester, 20% Bamboo Fiber

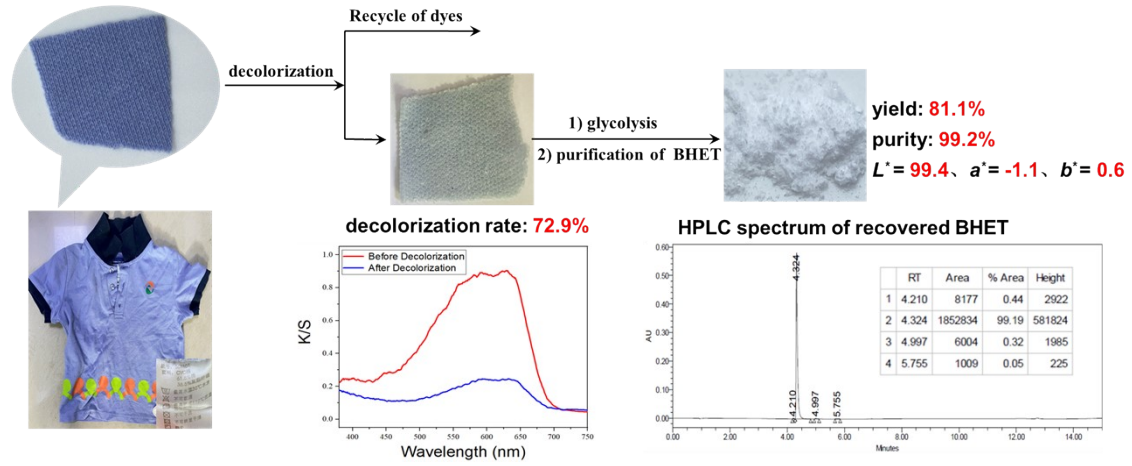


Chromaticity of recovered BHET:

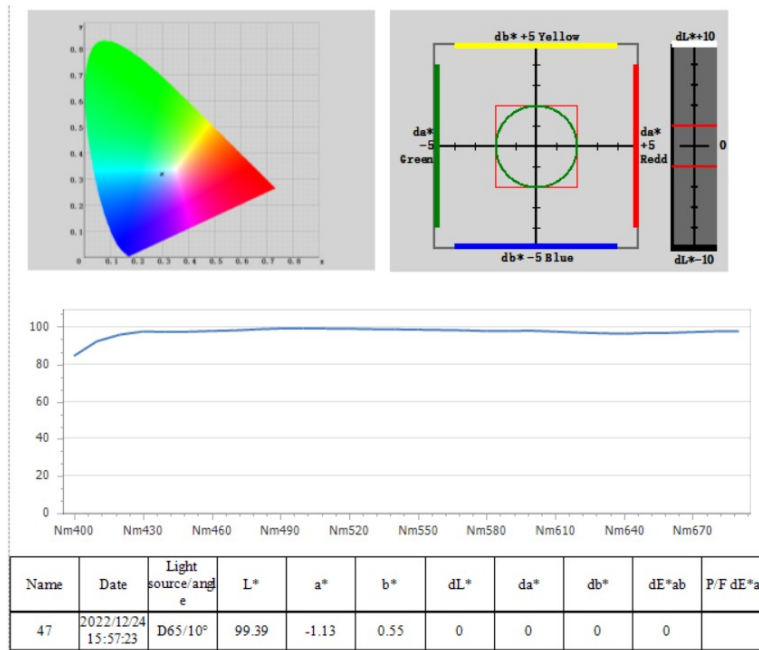


3.47 Sample 47

Composition: 38.5% Polyester, 61.5% Bamboo Fiber

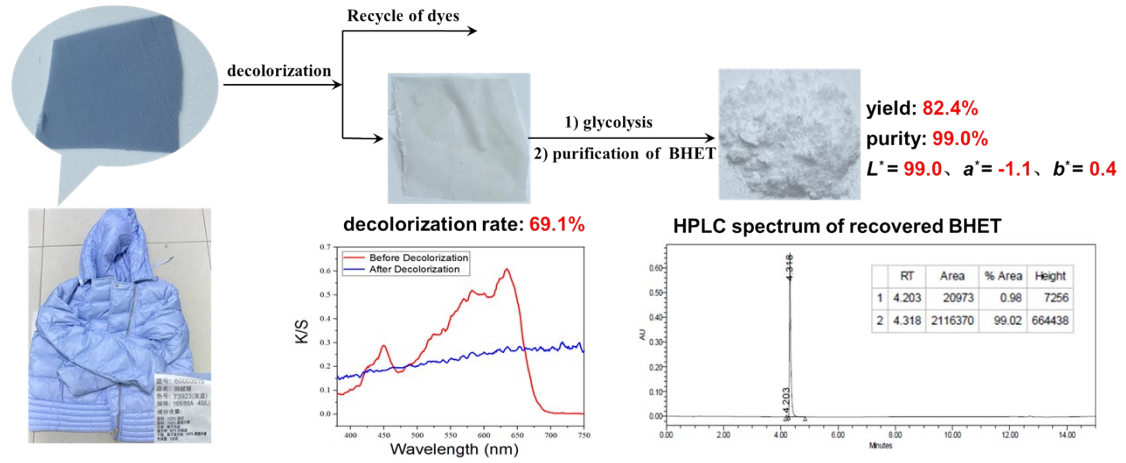


Chromaticity of recovered BHET:

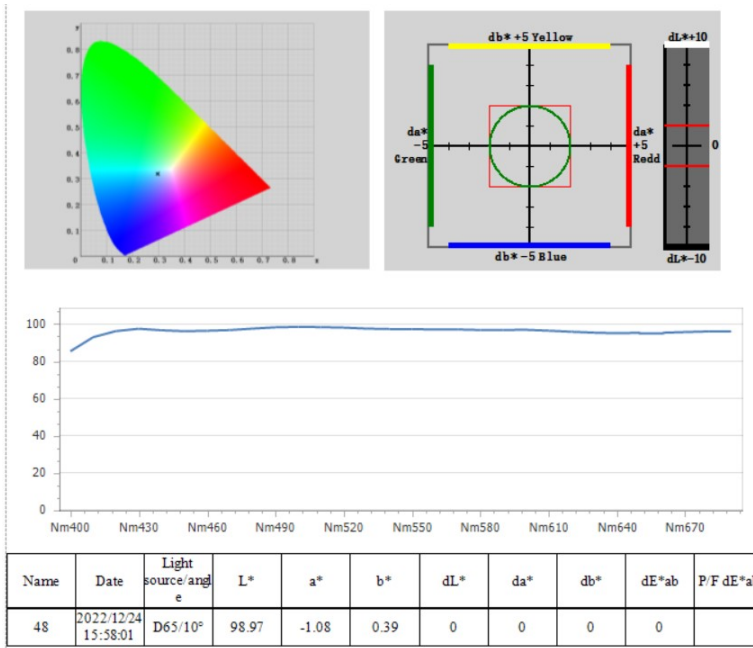


3.48 Sample 48

Composition: 100% Polyester

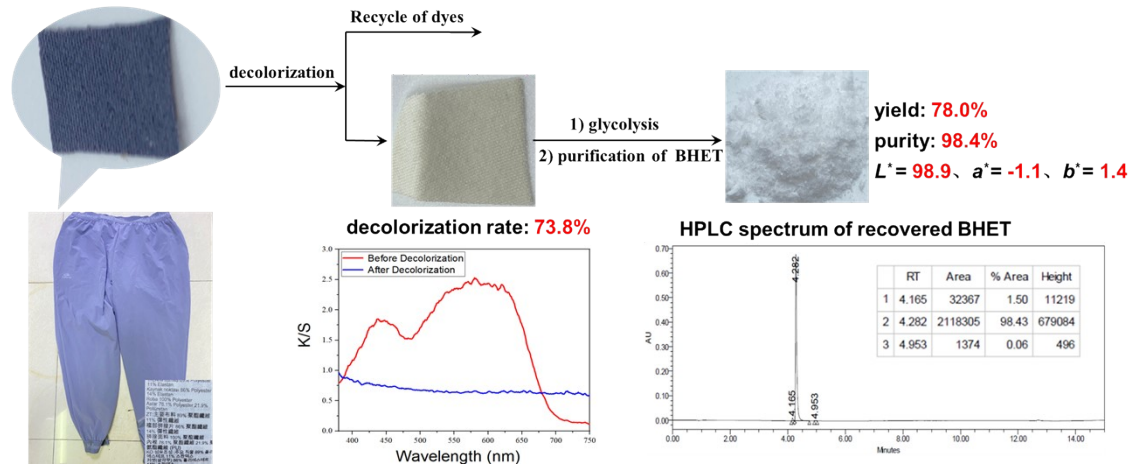


Chromaticity of recovered BHET:

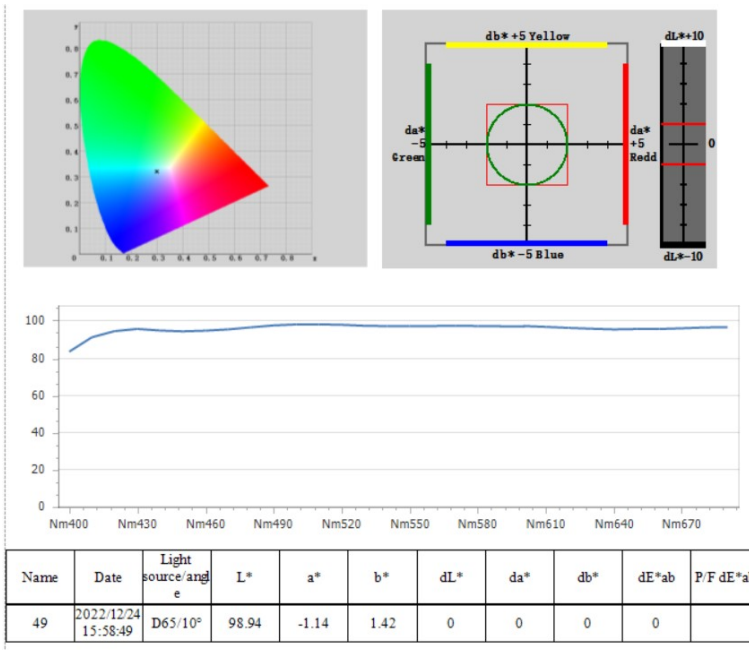


3.49 Sample 49

Composition: 89% Polyester, 11%Spandex

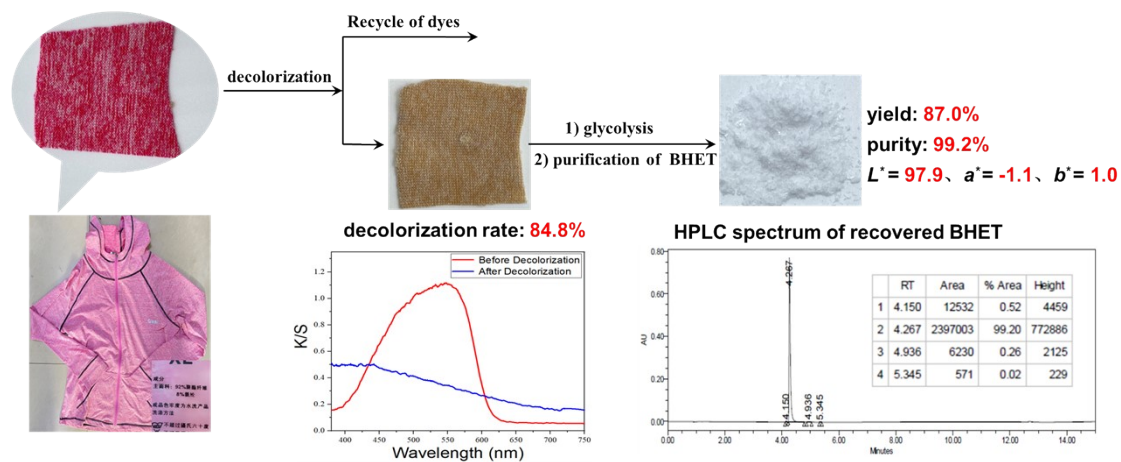


Chromaticity of recovered BHET:

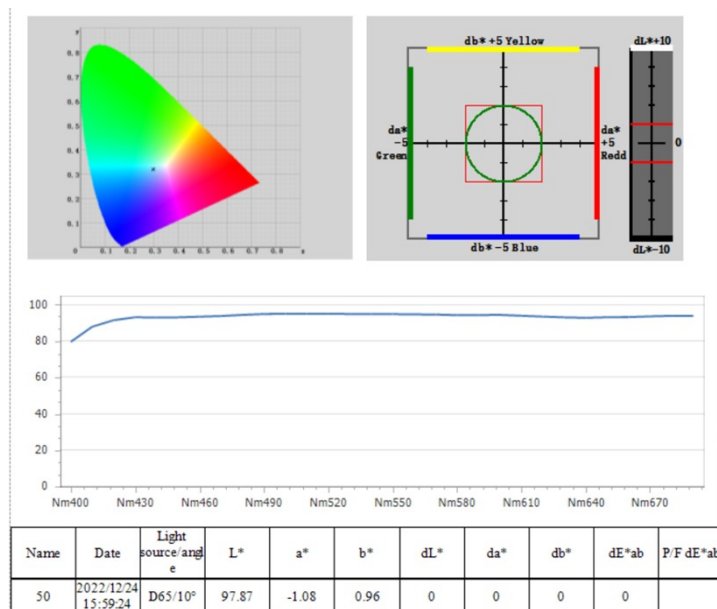


3.50 Sample 50

Composition: 92% Polyester、8%Spandex



Chromaticity of recovered BHET:



References

- Guanglin Luo HG, Haimei Wang. Gravure printing ink color matching method based on double constant Kubelka-Munk theory. *Packaging Engineering* **06**, 12-14 (2006).
- Byrd EFC, Rice BM. Improved Prediction of Heats of Formation of Energetic Materials Using Quantum Mechanical Calculations. *The Journal of Physical Chemistry A* **110**, 1005-1013 (2006).
- Gabitova AR, Kurdyukov AI, Gumerov FM, Ofitserov EN. DFT Study of Transesterification and Hydrolysis of the Fatty Acid Triglycerides, Carried Out under Supercritical Fluid Conditions. Analysis of Thermochemistry and Kinetics. *Journal of Engineering and Applied Sciences* **15**, 460-467 (2019).