Supporting Information

One-Component Antiaging Agents

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Experimental Section/Methods

Materials

7-Hydroxycoumarin (98%) and horseradish peroxidase (HRP, > 300 units/mg) were supplied by Aladdin Industrial Co., Ltd. (Shanghai, China). 6,7-dihydroxycoumarin (98%) was bought from Energy Chemical (Shanghai, China). 4-Methylumbelliferone (98%) and 2-Tert-Butyl-6-(5-Chloro-2H-Benzotriazol-2-yl)-4-Methylphenol (UV326, 98%) were obtained from Adamas Reagent Co., Ltd. (Shanghai, China). 2,2-Diphenyl-1-picrylhydrazyl (DPPH, 95%) was purchased from Alfa Aesar. 2, 2'-Azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) (ABTS, 98%) was supplied by Tokyo Chemical Industry (Shanghai, China). Thermoplastic polyurethane (TPU, WHT-1190) was provided by Wanhua Chemical (Yantai, China); Polyvinyl alcohol 1799 (PVA 1799, 98%), glycerin (99%),

acetonitrile (99%), methanol (99.5%), ethanol (99.7%), H_2O_2 (30%), NaOH (98%), 1,4-dioxane (99.5%), oxalic acid (99%), saturates barium chloride (99%), saturates calcium chloride (96%), 2,6-dichlorophenolindophenol (97%), trichloroacetic acid (99%), 2-thiobarbituric acid (98%), rhodamine B (reagent grade) and phenolphthalein (reagent grade) were purchased from Kelong Chemical Reagent Co., Ltd. (Chengdu, China). Malonaldehyde bis (diethyl acetal) (97%) was acquired from Macklin Chemicals (Shanghai, China). *Kyoho* grapes and *Millennium* cherry tomatoes were purchased from a local fruit supermarket and selected a similar size and color without mechanical damage. PE cling film was bought from a local market with a O_2 transmission rate of 25600 cm±20%/ (m^2 24 h atm), CO_2 transmittance of 89,000 cm±20%/ (m^2 24 h atm) and water vapor transmittance of 66 g±20%/ (m^2 24 h).

Fabrication and characterization of poly(coumarin) NPs:

Poly (7-hydroxycoumarin, HC) NPs (NP-1), poly (4-methylumbelliferone, MU) NPs (NP-2) and poly (6,7-dihydroxycoumarin, DHC) NPs (NP-3) were all synthesized by enzyme-induced polymerization method, with slight differences in details. Both NP-1 and NP-2 followed the same procedures. Taking NP-1 as an example, 90 mg HC was thoroughly dissolved in 18 mL deionized water and 12 mL acetonitrile. Various concentrations of HRP (10 mg/mL) were then added and stirred for 10 min. The reaction solution became purple after a certain amount of 30% H_2O_2 (10 mg/mL) was gradually added (keeping the mass ratio of HRP/30% H_2O_2 at 1/13). The solution turned dark brown after 6 h agitation at room temperature. The brown powder obtained after centrifugation (14000 r/min, 8 min), washing and freeze-drying for 48 h. For NP-3, the main difference was the solvent, and the specific experimental conditions were shown in Table S1-S2.

Preparation and characterization of polymer/poly(coumarin) NPs composite films:

TPU/poly(coumarin) NPs composite film: Firstly, a certain number of NPs or UV326 and AO1010 were accurately weighed into 94 g of 1, 4-dioxane, ultrasonically dispersed for 30 min, and then 6 g of TPU was added into it. Swelled overnight at room temperature and stirred under a metal bath at 60 ℃ for 2 h to obtain the mixed film solution. After cooling, 30 g were weighed and poured into a 20 cm×20 cm glass plate and dried at 50 ℃ for 4 h to produce a TPU-based composite film. According to the different types and contents of additives, they were named TPU-I (i=0-8). The specific formula was shown in Table S5, where the percentage content of the additive refers to its percentage of the dry matter of TPU.

PVA/poly(coumarin) NPs composite film: 6 g PVA powder was added to 90 g deionized water, which swelled overnight at room temperature and then stirred in an oil bath at 120 ℃ for 6 h to obtain PVA solution. After cooling, the solution was mixed with 4 mL suspension containing a certain number of NPs or UV326 and AO1010 (ultrasonic dispersion for 30 min), and 2% glycerin was added, stirred for 30 min weighed 30 g into 20 cm×20 cm acrylic plate and dried at 50 ℃ for 12 h to obtain PVA-based composite film. They were named PVA-i (i=0-8) according to the type and content of additives. The specific formula was shown in Table S6, where the percentage content of the additive refers to its percentage of the dry matter of PVA.

Photoaging process: In order to study the anti-photoaging effect of poly(coumarin) NPs on polymers, the prepared composite films were placed in a homemade UV aging chamber for accelerated photoaging experiments. The temperature was set at 35±2 °C, the sample size was 80 mm×60 mm, the distance between the sample and light source (500 W, 365 nm) was set to 20 cm, and the irradiation intensity was 22±2 W/m^2. Some of the samples were taken for testing at intervals of 0 h, 24 h, 48 h, 120 h and 240 h respectively. Aging under these conditions for 240 h was equivalent

to aging under natural conditions for about 6 years.

Characterization: The surface microstructure of NPs and films was observed under Nova Nano SEM 450 microscope. Films were directly attached to the conductive adhesive and the NPs were diluted with deionized water and dropped on mica flakes after 10 min of sonication, and then sputtered with gold for 90-120 s after drying. What's more, the microstructure of films was observed by atomic force microscopy (AFM, SPM 9600) in dynamic mode at room temperature. Each sample was scanned at a scanning rate of 1 HZ. The particle size distribution and zeta potential of the NPs in deionized water were measured using a dynamic laser scattering instrument (Malvern Nano ZS ZEN3690). The Fourier Transform Infrared Spectroscopy (FTIR) of the NPs were measured by KBr pellet method with a resolution of 4 cm^{-1} and a scan range of 4000~400 cm^{-1} to track changes in the material structure before and after polymerization. FTIR spectra of films were measured by Attenuated Total Reflection (ATR) method. The absorbance properties of NPs (20 μg/mL, ethanol) and films (10 mm×60 mm) were measured using a PerkinElmer Lambda 35 UV-Vis spectrophotometer in a wavelength range of 200 to 800 nm with a slit width of 2 nm. The thermal stability of the NPs and films was tested by scanning from 35 to 800 ℃ with a NETZSCH STA 449C TGA analyzer in N_2 or air atmosphere at a heating rate of 10 °C/min and a sample mass of 3 to 8 mg. Thermo Scientific K-Alpha+ X-ray photoelectron spectroscopy (XPS) was used to examine the chemical structures of the NPs surfaces. The reaction liquid was freeze-dried following the addition of H_2O_2 to induce the polymerization for 5 min, and the Electrospray Ionization Mass Spectrometry (ESI-MS) spectra of the material fragments were determined by negative ion mode electrospray ionization (Applied Biosystems API 2000). Mechanical properties were carried out on INSTRON universal material experimental machine according to ISO 527-2. The films were tested at a tensile rate of 20 mm/min.

Each sample was tested 5 times and the average value was used as the final data. The permeability coefficient of O_2 and CO_2 of films was measured by a VAC-V2 differential pressure method gas permeameter. The hydrophilicity of films was characterized by measuring the water contact angle (WCA) with a goniometer (Data-Physics OCA 25) at room temperature (20±1 °C) by dropping 8 μL water droplets onto the surface of films. In accordance with our prior research, the NPs' capacity to scavenge radicals was assessed utilizing the DPPH and $ABTS^{+\cdot}$ test technique.[1] The free radical scavenging ability of films was tested with reference to the method of Zhao et al.[2]

UV-shielding performance of composite films

The UV protection factor (UPF), UVB shielding efficiency, UVA shielding efficiency and UV shielding at 400 nm of each film were calculated according to the following formulas:

$$UPF = \frac{\sum_{\lambda=290}^{\lambda=400} E(\lambda) \times \varepsilon(\lambda) \times \Delta(\lambda)}{\sum_{\lambda=290}^{\lambda=400} E(\lambda) \times T(\lambda) \times \varepsilon(\lambda) \times \Delta(\lambda)}$$

$$UVB\ shielding\ efficiency\ (\%) = \left[1 - \frac{1}{k}\sum_{\lambda=290}^{315} T(\lambda)\right] \times 100\%$$

$$UVA\ shielding\ efficiency\ (\%) = \left[1 - \frac{1}{m}\sum_{\lambda=315}^{400} T(\lambda)\right] \times 100\%$$

$$UV\ shielding\ at\ 400\ nm = \left(1 - T_{400}\right) \times 100\%$$

Where $E(\lambda)$ is the sunlight spectral irradiance ($W \cdot m^{-2} \cdot nm^{-1}$), ε(λ) is the relative erythema effect, $\Delta(\lambda)$ is the wavelength interval, $T(\lambda)$ is the spectral transmittance of the films at the wavelength of λ, m and k are the measurement times between 290~315 nm and 315~400 nm, respectively.

The photocatalytic degradation of Rhodamine B solution containing Nano-TiO_2 under a UV lamp was studied to further evaluate the UV-shielding performance of the composite films. Slightly

modified according to Wang et al. 's method.[3] Briefly, 15 mL 1×10^{-5} M Rhodamine B solution was added into 20 mL brown bottle with 3 mg Nano-TiO_2 as photocatalyst and stirred in the dark for 30 min to reach adsorption/desorption equilibrium. The brown bottle's top was then sealed with the composite film, which was then exposed to UV radiation (365 nm) while being stirred. The variation in absorbance of Rhodamine B solution at 552 nm was detected by spectrophotometer. The UV shielding performance (I) of the composite film was calculated by the formula below:

$$I = \frac{A_t}{A_0} \times 100\%$$

Where A_0 and A_t are the absorbance of Rhodamine B solution without UV radiation and when the irradiation time is t, respectively.

Water vapor permeability (WVP)

WVP was performed according to the methods of ASTM E96/E96M-2014 and Zhou et al.[4] with slight modifications. Weighed (15.0±0.5) g of calcium chloride desiccant into the measuring cup to ensure RH=0% in the measuring cup, and sealed the films to be measured on the measuring cup mouth with sealing glue. All cups were then placed in a drying tower containing saturated sodium chloride for 24 d to ensure a stable osmotic state. The mass of the measuring cup was weighed every three days during this period and the WVP (unit: g Pa^{-1} s^{-1} m^{-1}) was calculated according to the following formula:

$$WVP = \left(\frac{\Delta w}{t}\right) \times \left(\frac{d}{A \times \Delta P}\right)$$

Where Δw is the change in the mass of measuring cup during test, g; t is the change in time corresponding to the mass change, s; d is the thickness of composite films, m; A is penetration area, m^2; ΔP is vapor pressure difference across the film sample, Pa.

Color and yellowing index

The L, a, and b values of these films before and after photoaging were determined by Color spectrum CS-6108 portable spectrophotometer using an Artificial Daylight 6500K (D65) light source and 10° viewing angle. The results were the average of 5 tests for each film. The total color difference (ΔE) of these films before and after photoaging was calculated by the following formula:

$$\Delta E = \left[(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2\right]^{0.5}$$

Where ΔL, Δa, and Δb are the differences of L, a and b values before and after the composite films aging, respectively.

The yellowness index (YI) was also tested by CS-6108 portable color spectrometer with standard C light source and 2° viewing angle, and YI (ASTM E313-2010) was selected to characterize the YI of the composite films. The yellowing index (ΔYI) was the difference of the YI of the composite films before and after aging. The data were averaged after each sample group was repeated 3 times.

Computational Methods

All optimizations were carried out in Gaussian16, Rev C.01[5] without constraints using the B3LYP[6,7] functional the 6-31G(d, p)[8,9] basis set. Grimme's empirical dispersion correction with Becke-Johnson damping[10] was added to address the noncovalent interactions. Vibrational frequencies were computed at the same level to obtain thermal corrections to Gibbs free energy (G_{corr}) and to characterize the transition states (one and only one imaginary frequency). The following single point calculations were carried out with a larger basis set, 6-311G (2d, p)[11], for more accurate electronic energies (E) and the Gibbs free energies are calculated as:

$$G = Gcorr\ (B3LYP/6-31G(d,p)) + E(B3LYP/6-311G(2d,p))$$

Transition state searches were performed to determine the potential barriers for the reaction of NP, AO1010 and TPU to peroxyl radicals, the energy barrier for the reaction being the energy

difference between the transition state and the reactant. Given the limitations of computational power, ROO· was chosen as the ethylperoxyl radical (EtOO·).

Fruits Application.

Two representative fruits, non-climacteric fruit *Kyoho* grapes and climacteric fruit *Millennium* cherry tomatoes, were selected to verify the effectiveness of composite films as packaging films for fruit preservation. The fruits were randomly divided into 6 groups, each group was about 2 kg. The fruits were packaged by heat-sealing method with composite films, with the unwrapped fruits were taken as blank group and the fruits encapsulated with PE plastic wrap were taken as control group, and stored at room temperature. Each index was tested at least three times at regular intervals.

Characterization: 10 fruits were randomly selected from each group, and the firmness of each fruit was measured using a hand-held GY-3 fruit penetrometer (kg/cm^2), and each fruit was tested 5 times. 10 fruits were randomly selected from each group. The edible parts were chopped and ground, and then the homogenized juice was squeezed out with gauze. The soluble solid content of fruit was measured by WYT (0-80%) refractometer. The titratable acid content of fruit was determined by the indicator titration method. The ground homogenate juice was measured with a pH meter, and the result was accurate to 0.01.

Respiration Rate: The respiration rate of fruit was determined by static alkali absorption method.[12] 10.0 mL 0.4 mol/L NaOH was accurately measured into the petri dish, then the petri dish was placed at the bottom of the respiration chamber (glass desiccator), a partition was placed, and filled it with about 200 g of fruits. After sealing for 1 h, the alkaline solution was transferred into a triangular flask

(rinsed for 3~4 times). The CO_2 produced was titrated with 0.2 mol/L oxalic acid solution by adding 1.0 mL of saturated $BaCl_2$ solution and 2 drops of phenol indicator. A blank titration was made in the same way. Respiration rate was expressed as the mass of CO_2 released per kg of fruit per hour by the following formula:

$$Respiration\ Rate = \frac{(V_1 - V_2) \times c \times 22}{m \times t}[mg/(kg \cdot h)]$$

Where c is the molar concentration of oxalic acid solution, mol/L; V_1 is the amount of oxalic acid solution in the blank titration, mL; V_2 is the amount of oxalic acid solution in determination titration, mL; m is the mass of fruit, kg; t is the determination time, h; 22 is the mass conversion number of NaOH to CO_2 in the determination (=44/2, 44 is the molar mass of CO_2, calculated according to the standard condition; 2 refers to the consumption of 2 M NaOH in the absorption process is equivalent to the absorption of 1 M CO_2).

Decay rate

The decay degree of fruit was graded according to the rotten area of fruit and calculated as formula:

Rot area rating

Grade	Phenomenon
0	No decay
1	The rotten area is less than 1/4 of the fruit area
2	The rotten area is less than 1/4~1/2 of the fruit area
3	The rotten area is less than 1/2~3/4 of the fruit

area

The rotten area is less than 3/4 of the fruit area

$$Decay\ rate\ (\%) = \frac{\sum X_i \times n_i}{X_m \times N} \times 100$$

where X_i is the decay grade of fruit; n_i is the number of fruits in this grade; X_m is the highest decay grade; and N is the total number of fruits.

Weight loss rate and Dropping rate

The mass of fruit on the day of picking was M_0, and the mass of fruit (M_t) was measured every 2 days. The weight loss rate was calculated as follows:

$$Weight\ Loss\ Ratio\ (\%) = \frac{M_0 - M_t}{M_0} \times 100$$

The weight of dropped grape berries (M_d) and the total weight of a bunch of grapes (M_b) were recorded for each test referring to the method of Chen et al.,[12] and the dropping rate was calculated according to the following formula:

$$Dropping\ rate\ (\%) = \frac{M_d}{M_b} \times 100$$

Ascorbic acid content

The specific steps for the determination of the ascorbic acid content were as follows: under the condition of dark, weighed 20 g fruit with the edible part and then mixed with 20 g oxalic acid solution (20 g/L) and ground into homogenate. Then transferred them into 100 mL volumetric flask and constant volume with oxalic acid, shook well. Added a certain amount of white clay and then filtered with filter paper due to the filtrate was red. Measured 10 mL of the filtrate with a pipette and titrated with a pre-calibrated 2,6-dichloroindophenol solution (titer T, mg/mL) until the filtrate turned pink

and did not fade within 30 s. Recorded the volume of solution (V, mL) consumed at this time. Meanwhile, recorded the volume of solution (V_0, mL) consumed by titrating 10 mL of oxalic acid (20 g/L) solution. The ascorbic acid content (X, mg/100 g) was calculated according to the following formula:

$$X = \frac{(V - V_0) \times T \times A}{m} \times 100$$

where A is the dilution factor; m is the fruit weight, g.

Malondialdehyde content

The 2-thiobarbituric acid (TBA) method was used to measure Malondialdehyde content (MDA), the end product of lipid peroxidation, according to the method of Chen et al. with slight modifications.[12]

Weighed 1.50 g (accurate to 0.01 g) cherry tomatoes flesh mixed with 7.5 mL of 100 g/L trichloroacetic acid (TCA) solution, ground into homogenate at low temperature, fully extracted for 20~30 min, centrifuged at 12000 rpm for 15 min at 4 °C. Accurately pipetted 2 mL of the supernatant and transferred to a stoppered test tube, and added 5 mL of 0.5% TBA (dissolved in 10% TCA), shook well and then placed in boiling water at 100 °C for 20 min. It was quickly cooled in ice water after taking out and centrifuged at 12,000 rpm for 5 min, the supernatant was taken to measure the absorbance at 450 nm, 532 nm and 600 nm, and the content of MDA was calculated as follows:

$$MDA\ Content\ (umol \cdot g^{-1}) = \left[6.45 \times \left(OD_{532} - OD_{600} \times OD_{450}\right)\right] \times V / \left(V_s \times m\right)$$

where V is the total volume of extract, mL; V_s is the volume taken during measurement, mL; m is the weight of cherry tomatoes flesh, g.

Statistical analysis

Final results were expressed as the mean ± standard deviation of multiple samples. Duncan's multiple difference analysis was performed using SPSS 22 software with ANOVA ($P<0.05$). Duncan's significance test showed that the same letter indicated no significant difference ($P>0.05$), while lowercase letters (a, b, c, etc.) indicated significant difference ($P<0.05$). Origin 2021 was used for data processing and drawing.

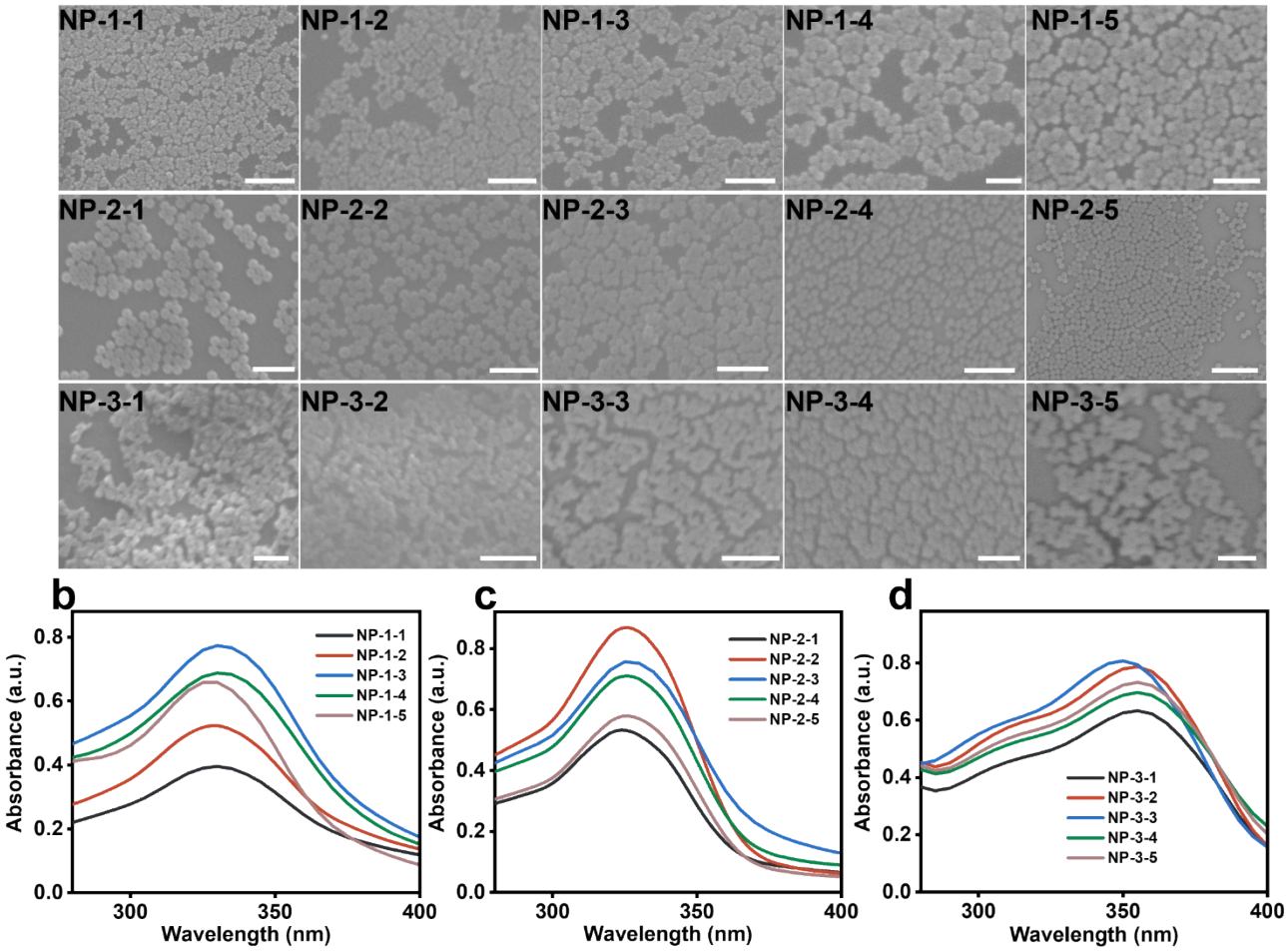


Figure S1 Representative SEM images of the resulting poly(coumarin) NPs in Table S1 and Table S2 (scale bar: 1 μm). b-d) UV spectra of the resulting poly(coumarin) NPs in Table S1 and Table S2.

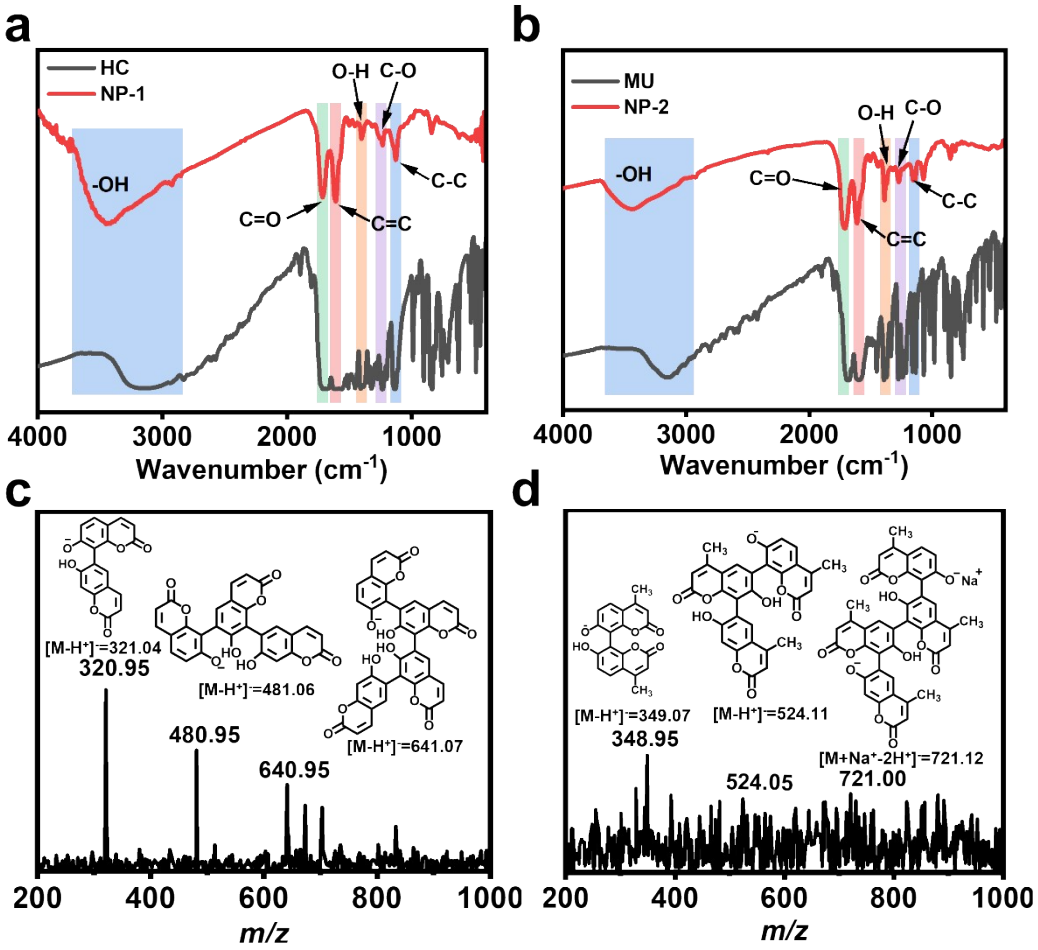


Figure S2 FTIR spectra of a) 7-hydroxycoumarin (HC) and NP-2, b) 4-methylumbelliferone (MU) and NP-2. ESI-MS spectra of the crude product of c) HC and d) MU polymerization reaction for 5 min and possible intermediate structures.

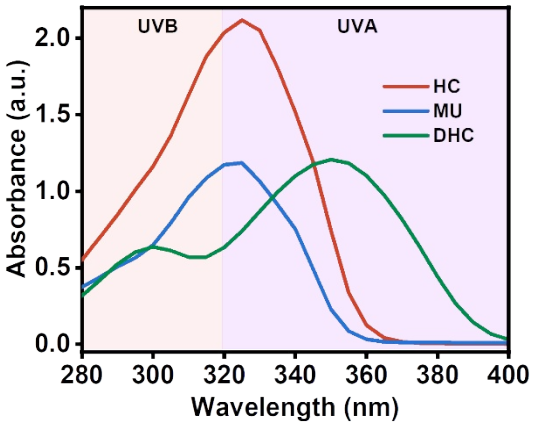


Figure S3 UV spectra of HC, MU and DHC coumarin monomers molecules (dissolved in anhydrous ethanol, 20 μg/mL).

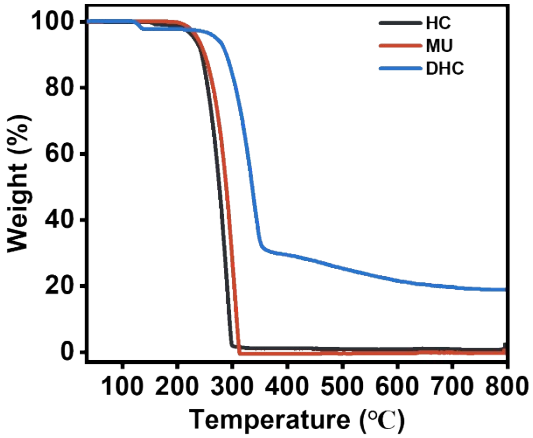
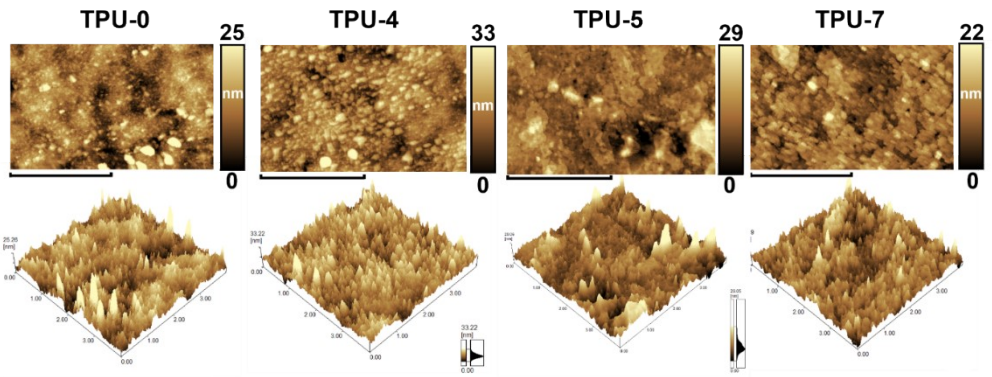


Figure S4 TGA curves of HC, MU and DHC coumarin monomers molecules under N_2.

a

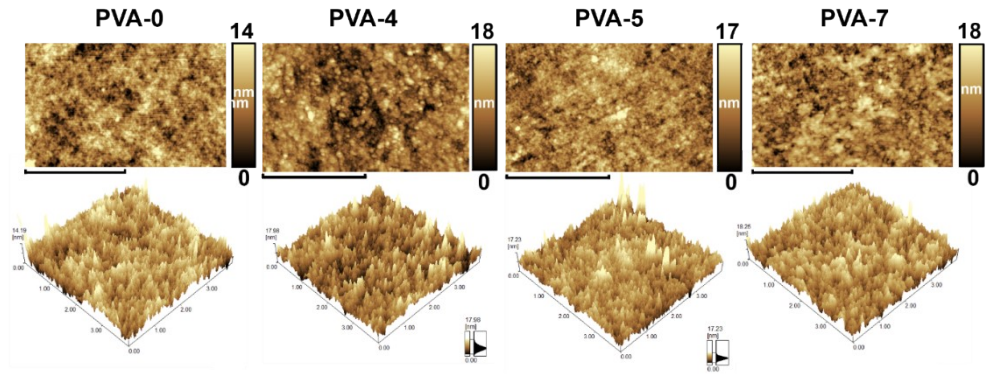


b

	TPU-0	TPU-4	TPU-5	TPU-7
Ra (nm)	3.89	4.59	3.86	2.89
Rq (nm)	5.31	5.96	5.38	3.73

Figure S5 a) AFM height images and corresponding 3D images of TPU-based composite films. b) Surface roughness parameters of the films (*Ra*: the arithmetic mean value of the surface roughness. *Rq*: root-mean-square roughness).

a



b

	PVA-0	PVA-4	PVA-5	PVA-7
Ra (nm)	2.21	2.58	2.39	2.64
Rq (nm)	2.82	3.32	3.21	3.30

Figure S6 a) AFM height images and corresponding 3D images of PVA-based composite films. b) Surface roughness parameters of the films (*Ra*: the arithmetic mean value of the surface roughness. *Rq*: root-mean-square roughness).

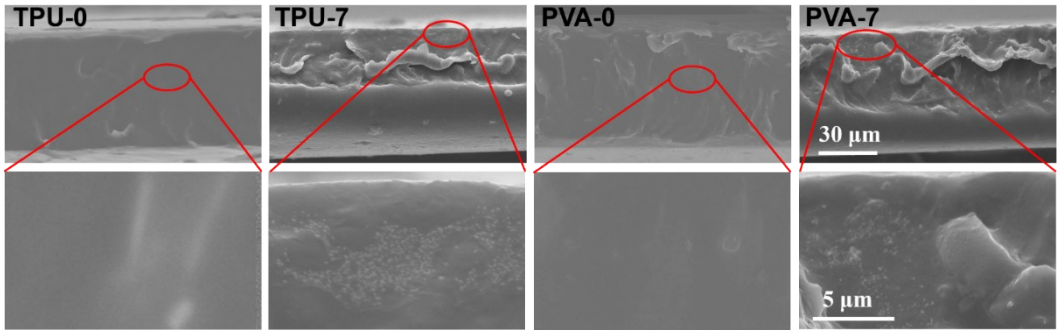


Figure S7 SEM images of cross section of TPU-0, TPU-7, PVA-0 and PVA-7 films.

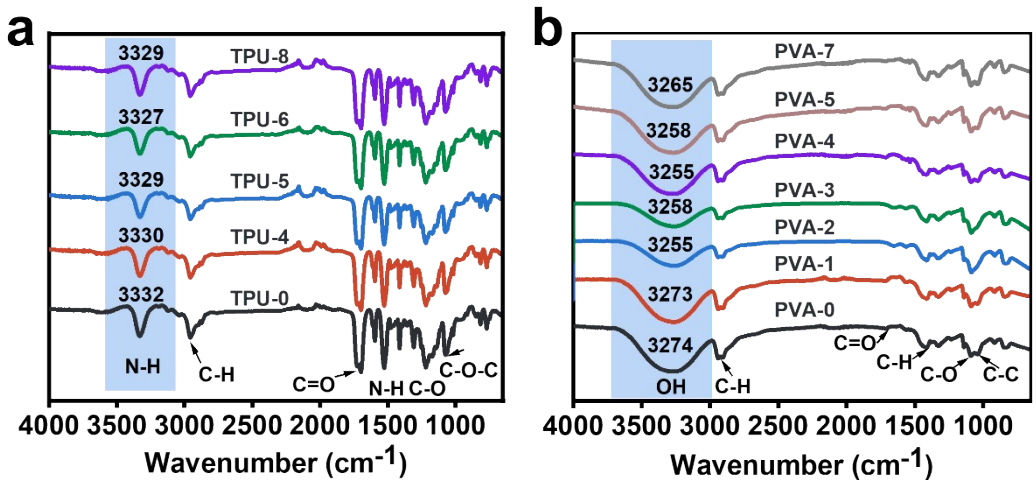


Figure S8 ATR-FTIR spectra of a) TPU-0 and different TPU-based composite films as well as b) PVA-0 and different PVA-based composite films.

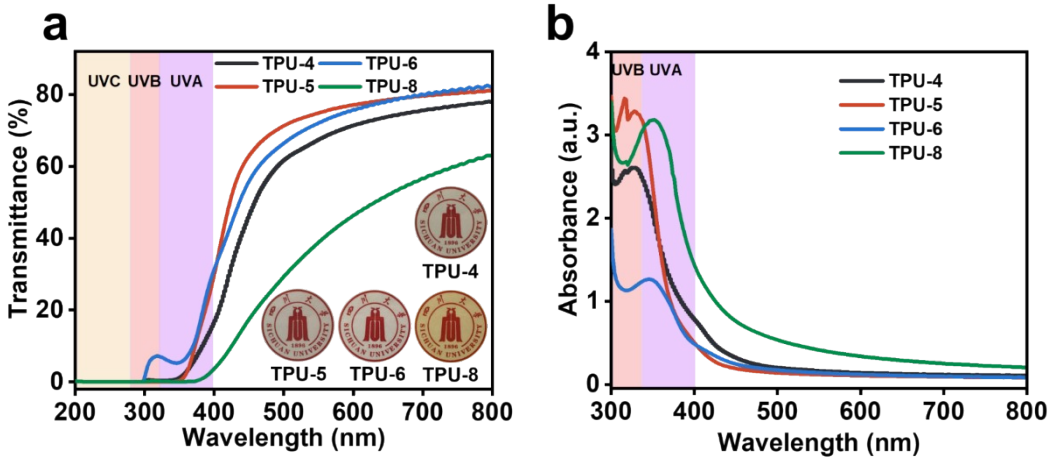


Figure S9 a) UV-Vis transmittance spectra and b) UV-Vis absorption spectra of TPU-0 and different TPU-based composite films (thickness: 60 μm).

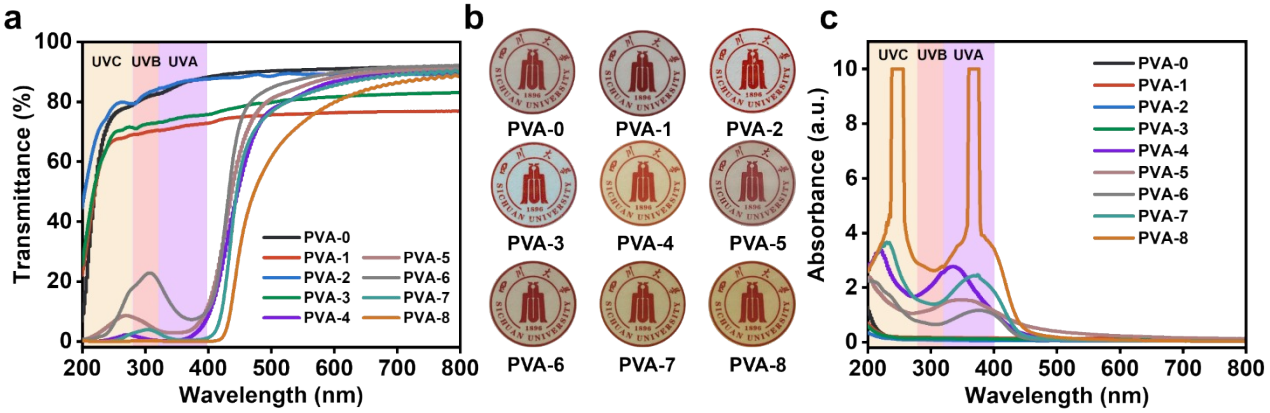


Figure S10 a) UV-Vis transmittance spectra, b) the photos and c) UV-Vis absorption spectra of PVA-0 and different PVA-based composite films (thickness: 60 μm).

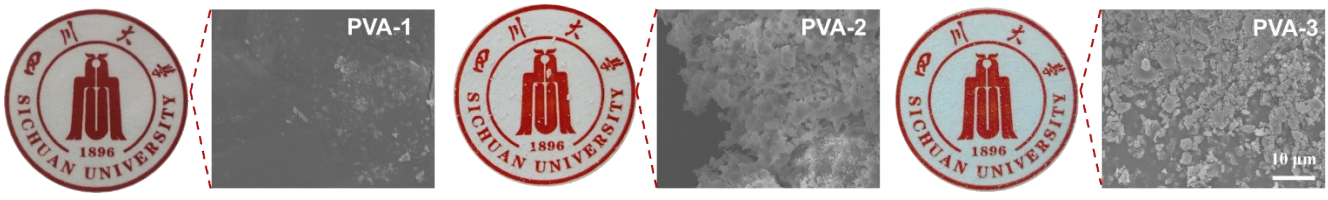


Figure S11 Typical photos and SEM results of PVA-i (i-1-3) films (scale bar: 10 μm).

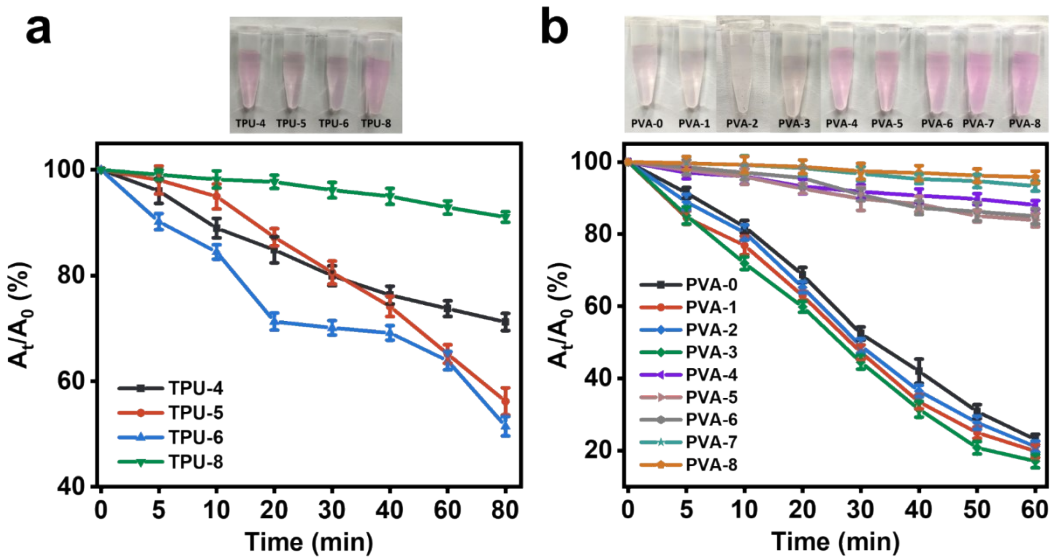


Figure S12 Photodegradation curves of Rhodamine B solutions protected by a) different TPU-based composite films as well as b) PVA-0 and different PVA-based composite films.

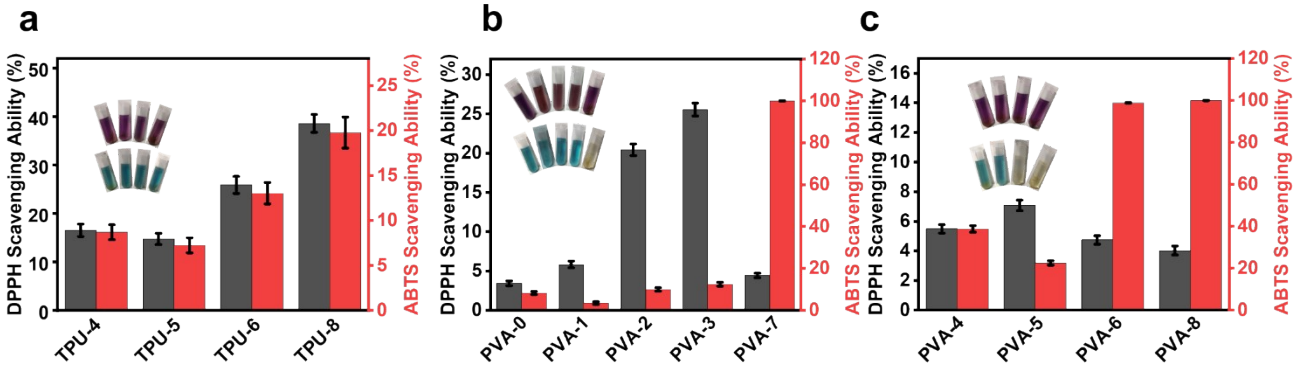


Figure S13 $ABTS^{+\cdot}$ and DPPH radical scavenging activities of a) different TPU-based composite films and b-c) PVA-0 and different PVA-based composite films.

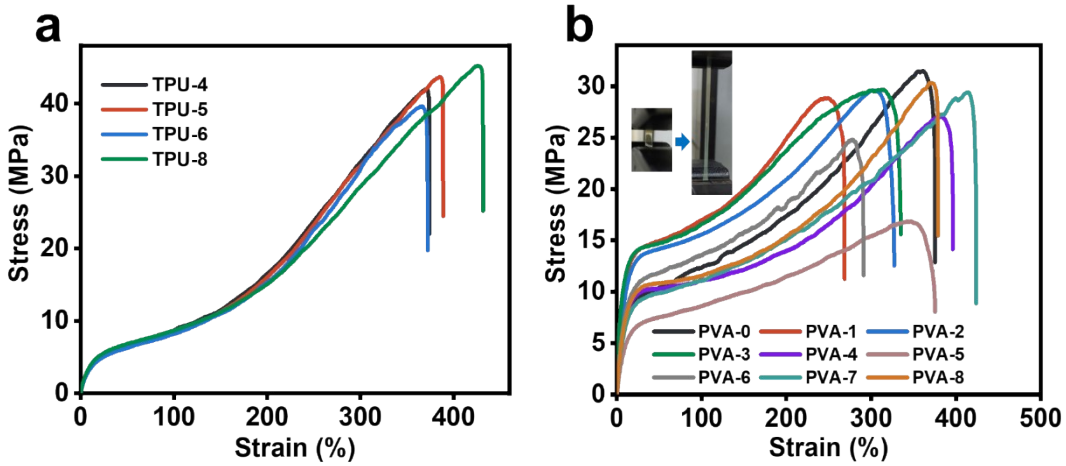


Figure S14 Typical stress-strain curves of a) different TPU-based composite films and b) PVA-0 and different PVA-based composite films.

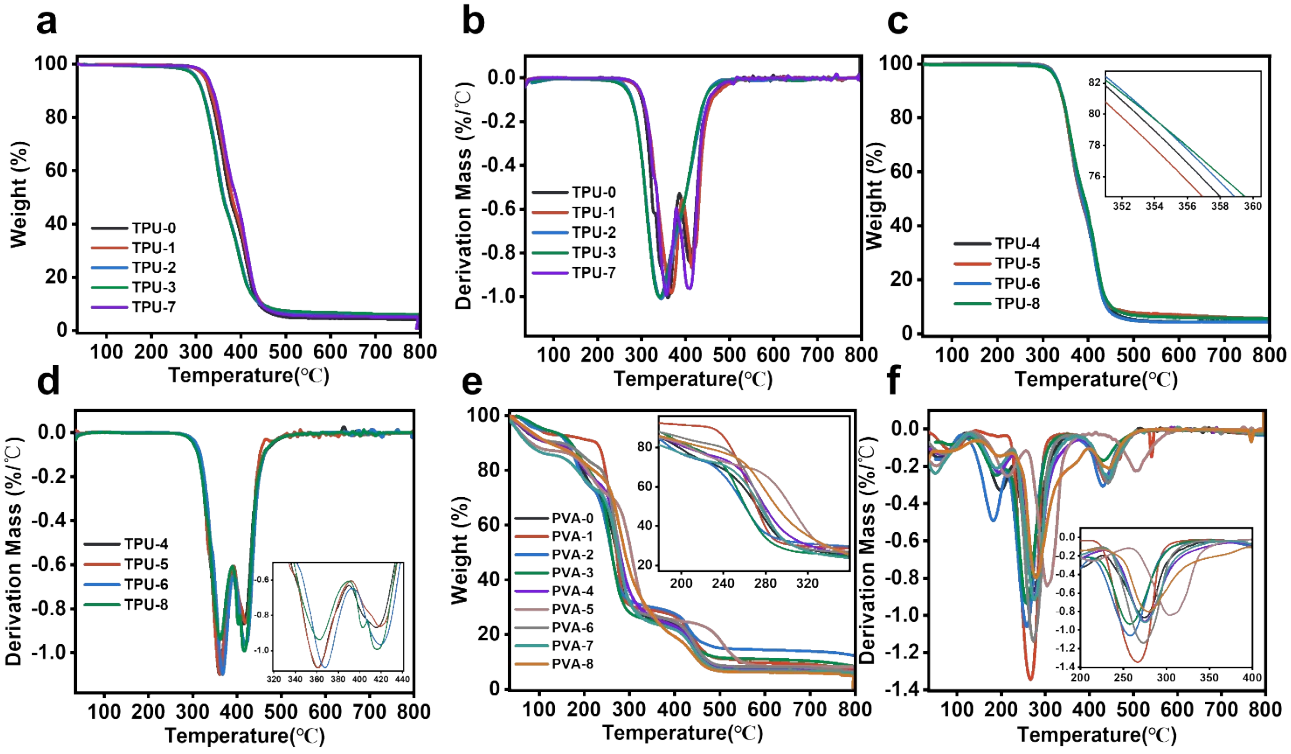


Figure S15 a-d) TGA and DTG curves of different TPU-0 and TPU-based composite films. e) TGA and f) DTG curves of PVA-0 and different PVA-based composite films.

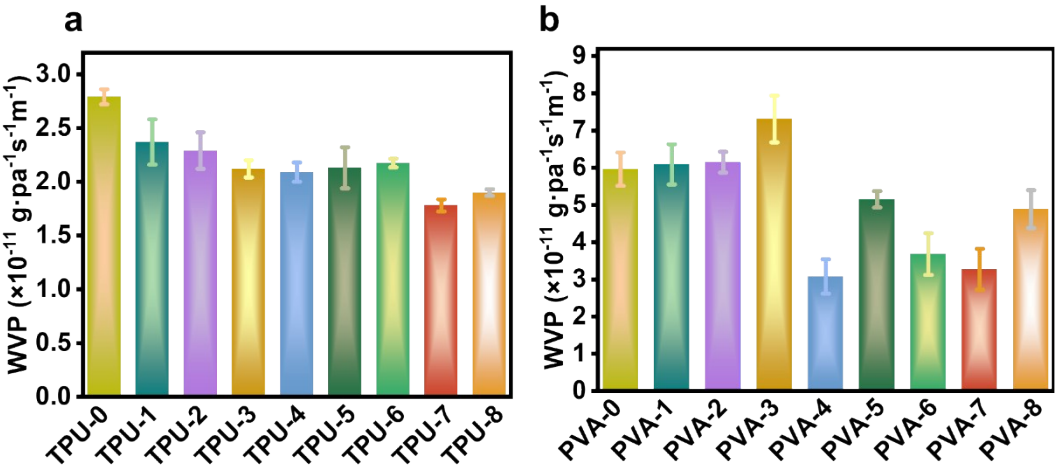


Figure S16 Water vapor permeability (WVP) of a) TPU-0 and different TPU-based composite films and b) PVA-0 and different PVA-based composite films.

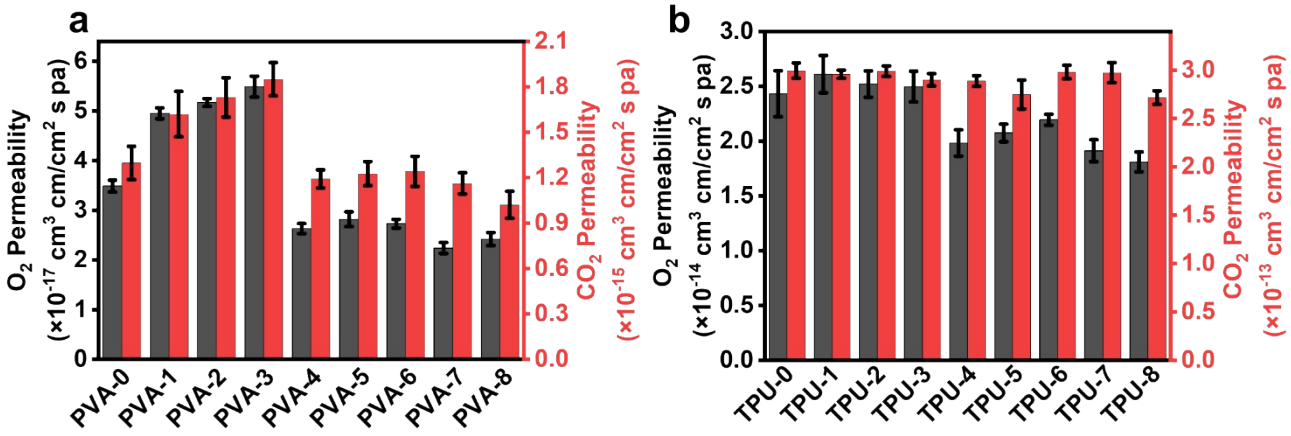


Figure S17 O_2 and CO_2 permeability of a) TPU-0 and different TPU-based composite films and b) PVA-0 and different PVA-based composite films.

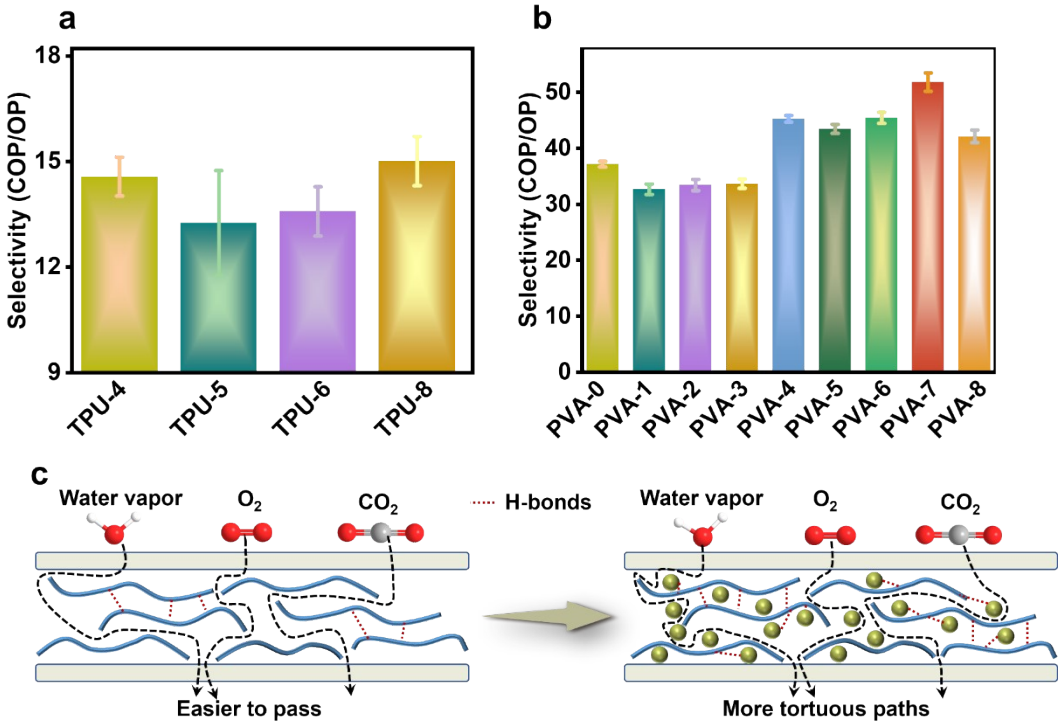


Figure S18 COP/OP selectivity of a) different TPU-based composite films and b) PVA-0 and different PVA-based composite films. c) Schematic diagram of water vapor, O_2 and CO_2 transmission.

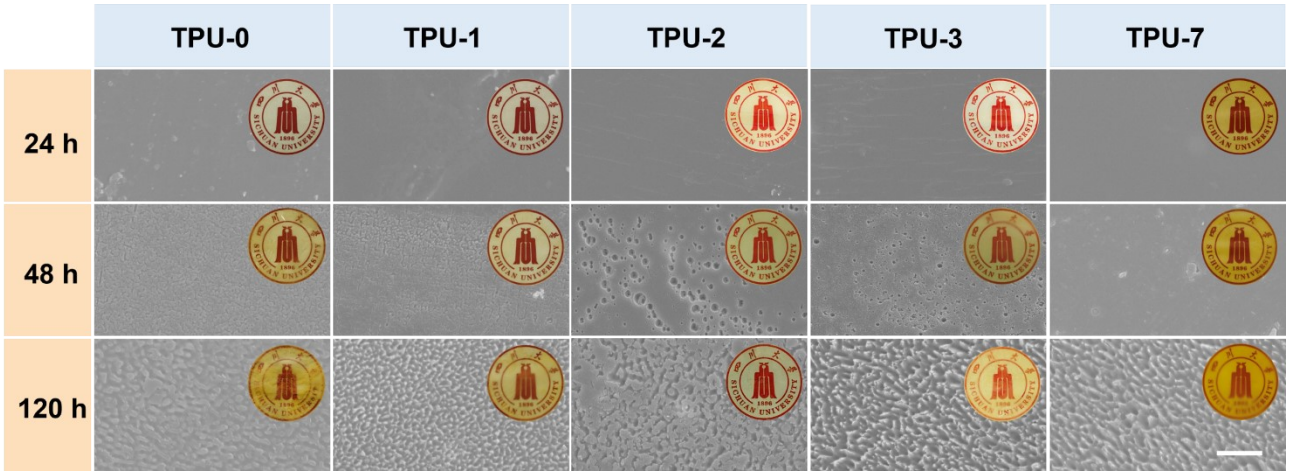


Figure S19 Typical SEM results of TPU-0 and different TPU-based composite films after different photoaging times (scale bar: 10 μm).

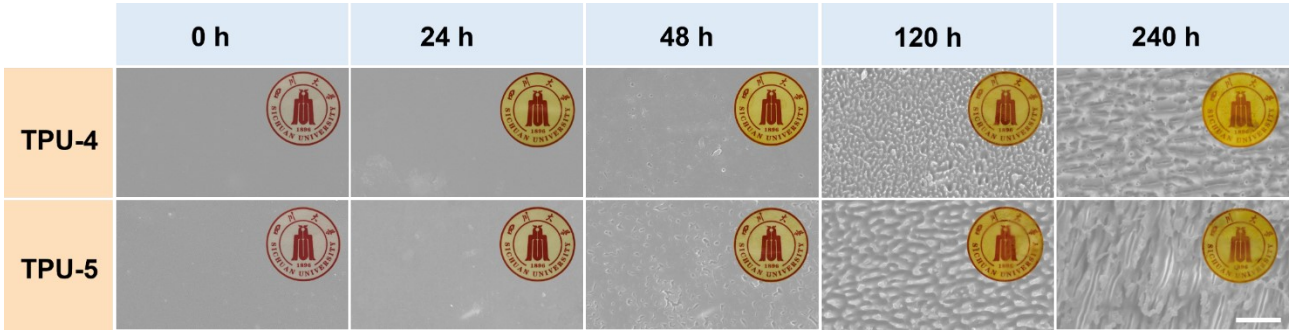


Figure S20 Typical SEM results of TPU-4 and TPU-5 composite films after different photoaging times (scale bar: 10 μm).

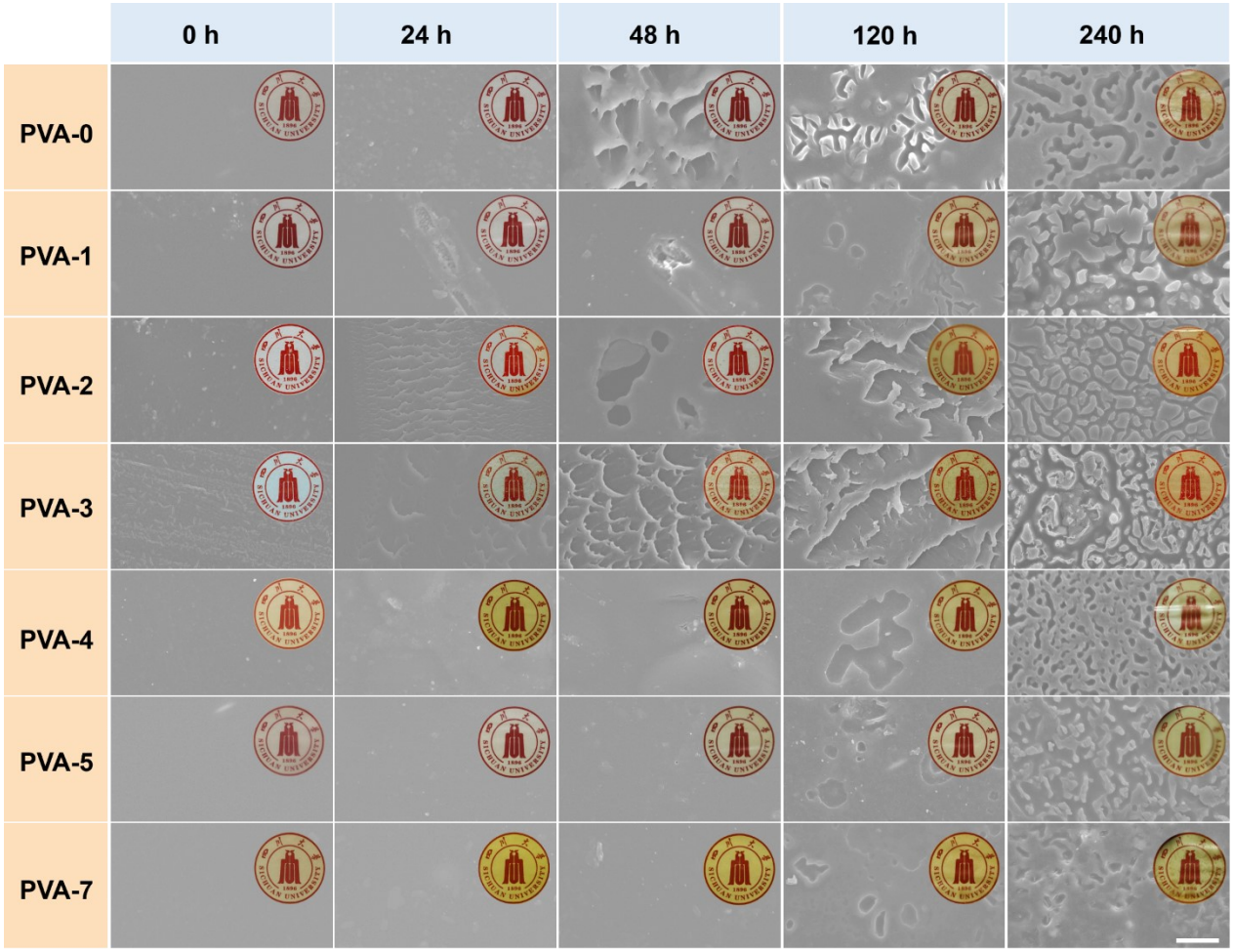


Figure S21 Typical SEM results of PVA-0 and different PVA-based composite films after different photoaging times (scale bar: 10 μm).

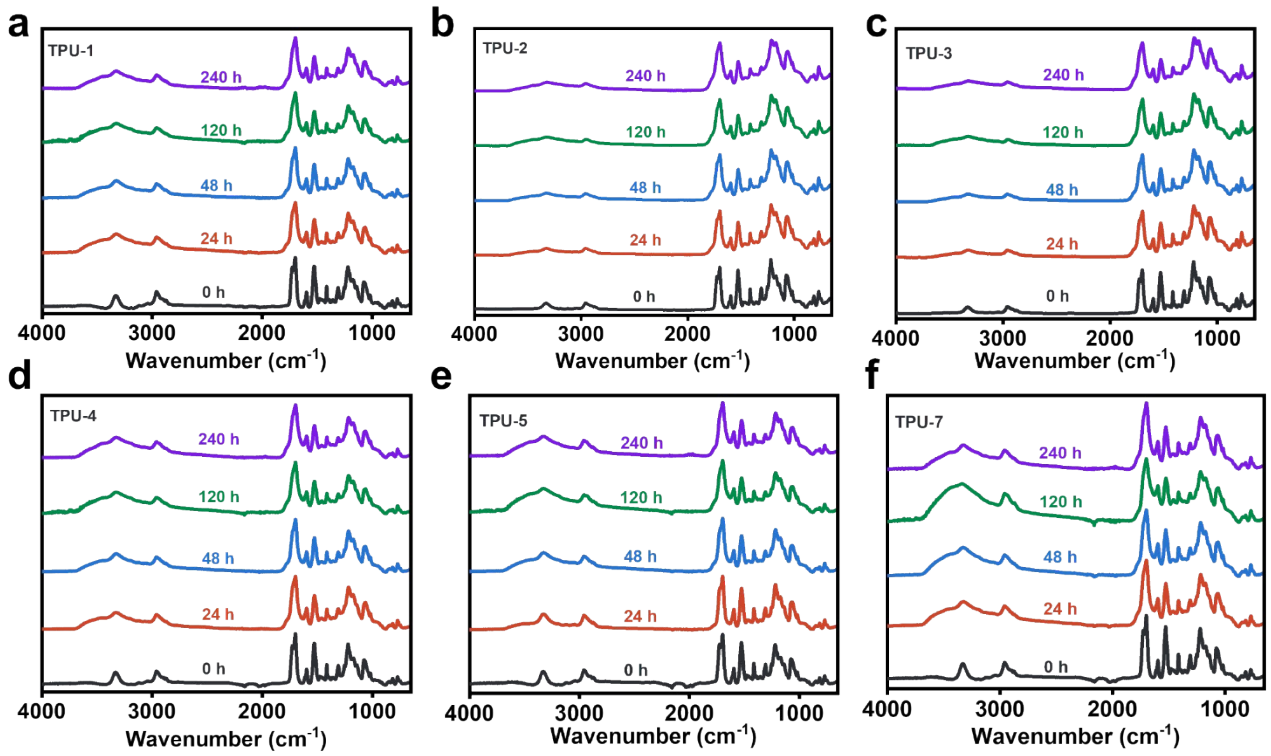


Figure S22 ATR-FTIR spectra of a) TPU-1, b) TPU-2, c) TPU-3, d) TPU-4, e) TPU-5 and f) TPU-7 films under different photoaging time.

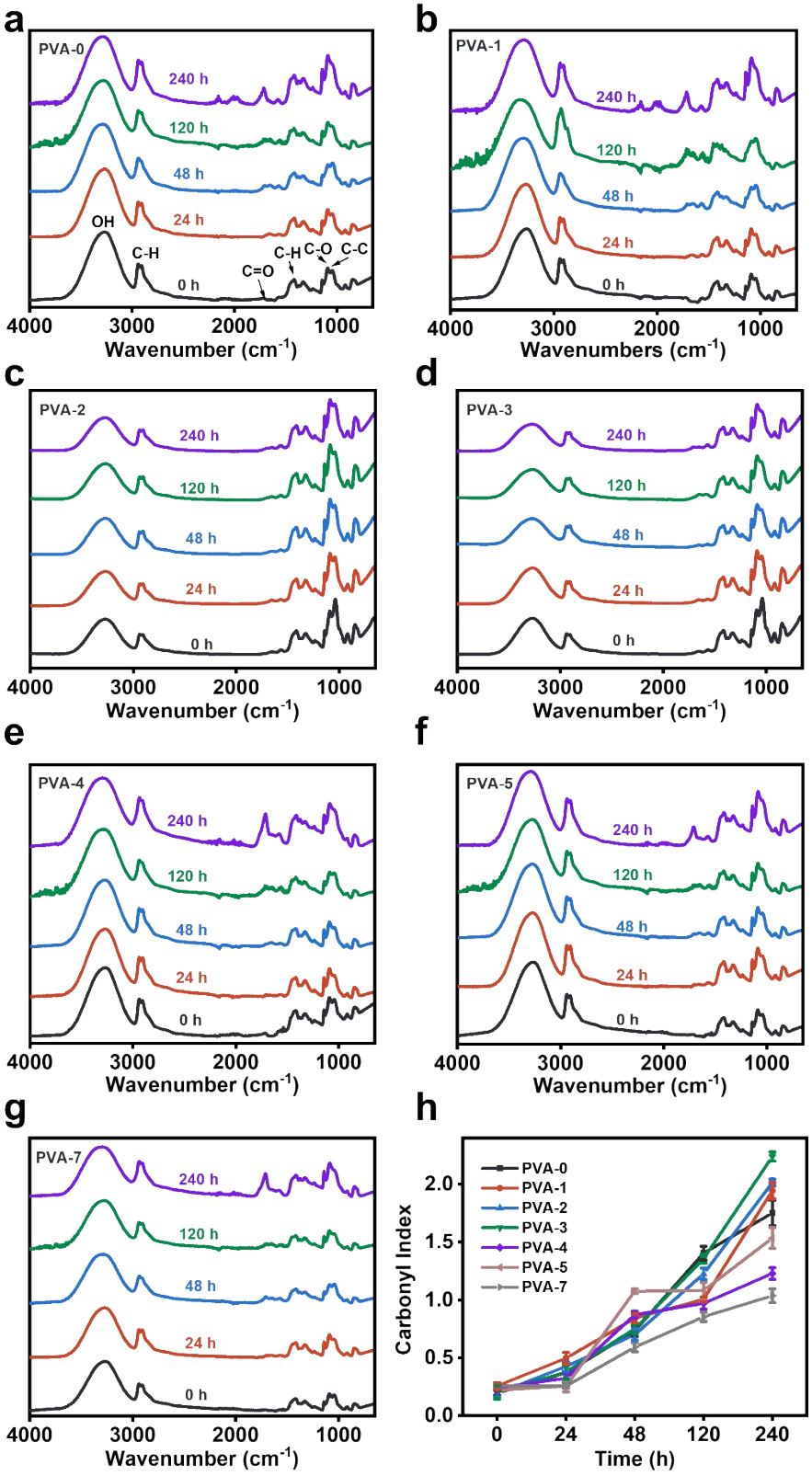


Figure S23 ATR-FTIR spectra of a) PVA-0, b) PVA-1, c) PVA-2, d) PVA-3, e) PVA-4, f) PVA-5 and g) PVA-7 films under different photoaging time. h) Changes in carbonyl index of PVA and different PVA-based composite films during photoaging.

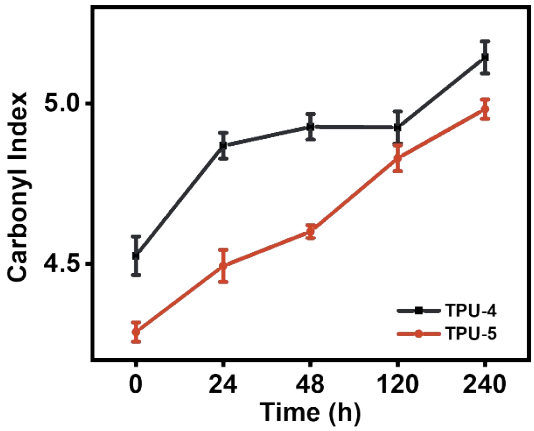


Figure S24 Changes in carbonyl index of TPU-4 and TPU-5 films during photoaging.

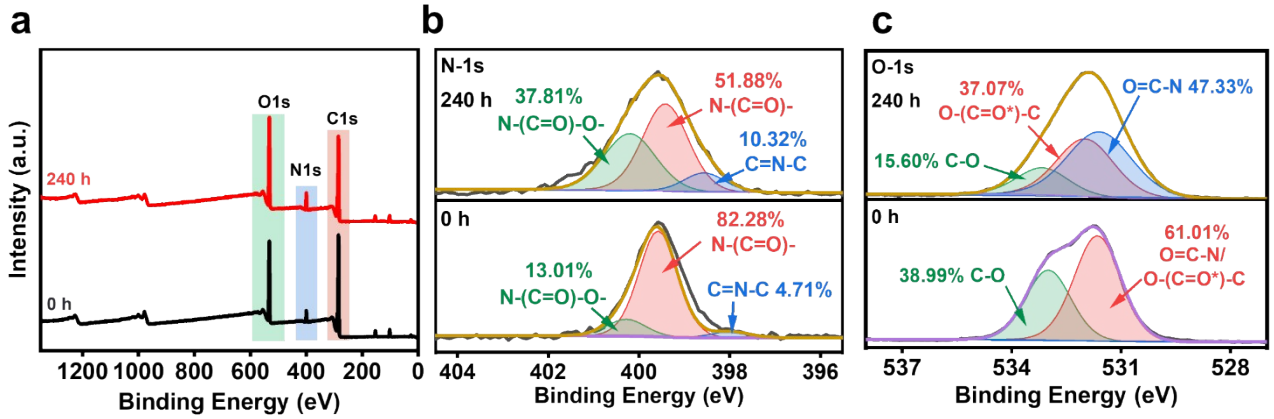


Figure S25 a) XPS spectra, b) N 1s, and c) O 1s high resolution spectra of TPU-7 before and after photoaging for 240 h.

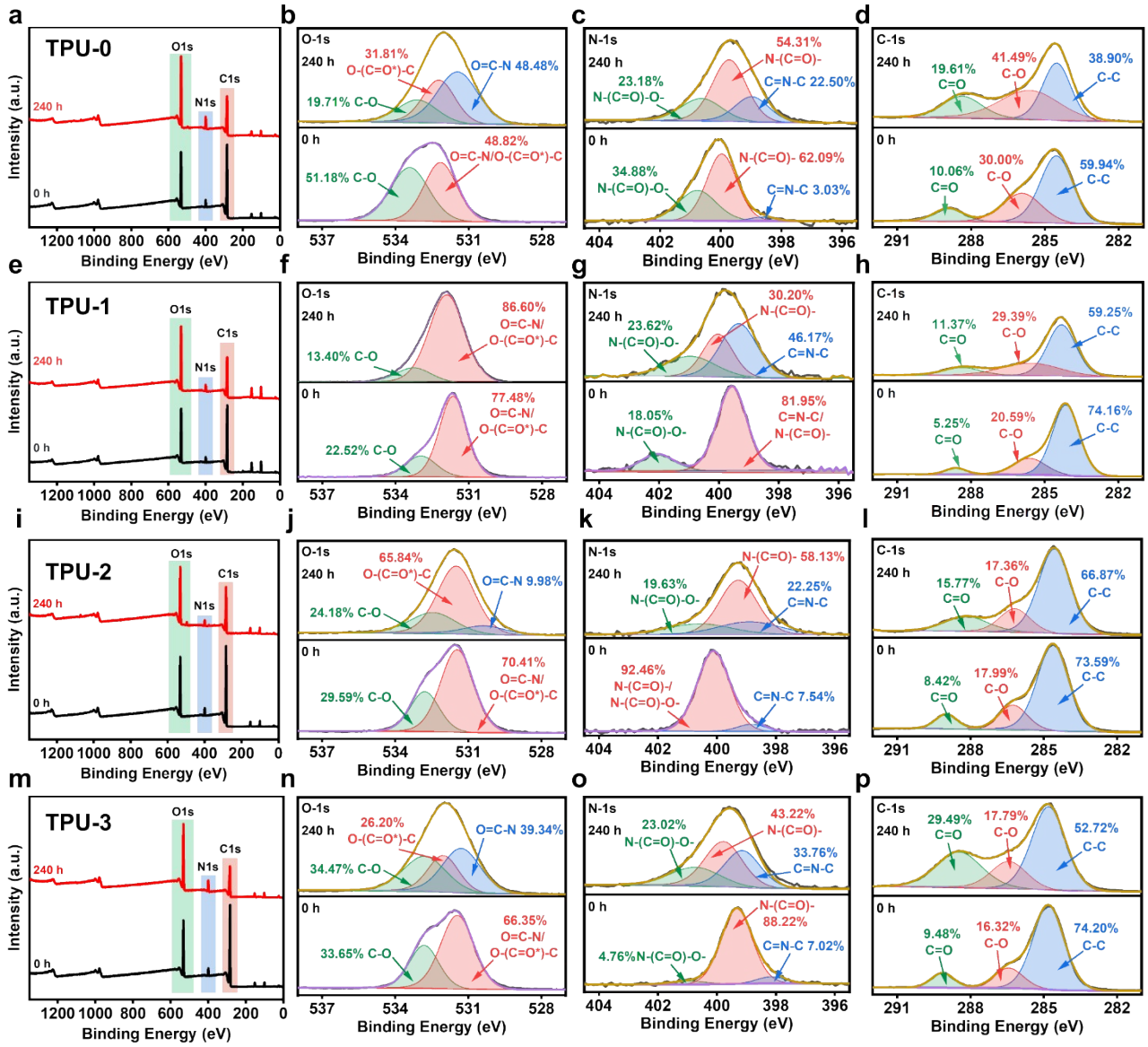


Figure S26 a) XPS spectra, b) O 1s, c) N1s and d) C 1s high resolution spectra of TPU-0 before and after photoaging for 240 h. e) XPS spectra, f) O 1s, g) N1s and h) C 1s high resolution spectra of TPU-1 before and after photoaging for 240 h. i) XPS spectra, j) O 1s, k) N1s and l) C 1s high resolution spectra of TPU-2 before and after photoaging for 240 h. m) XPS spectra, n) O 1s, o) N1s and p) C 1s high resolution spectra of TPU-3 before and after photoaging for 240 h.

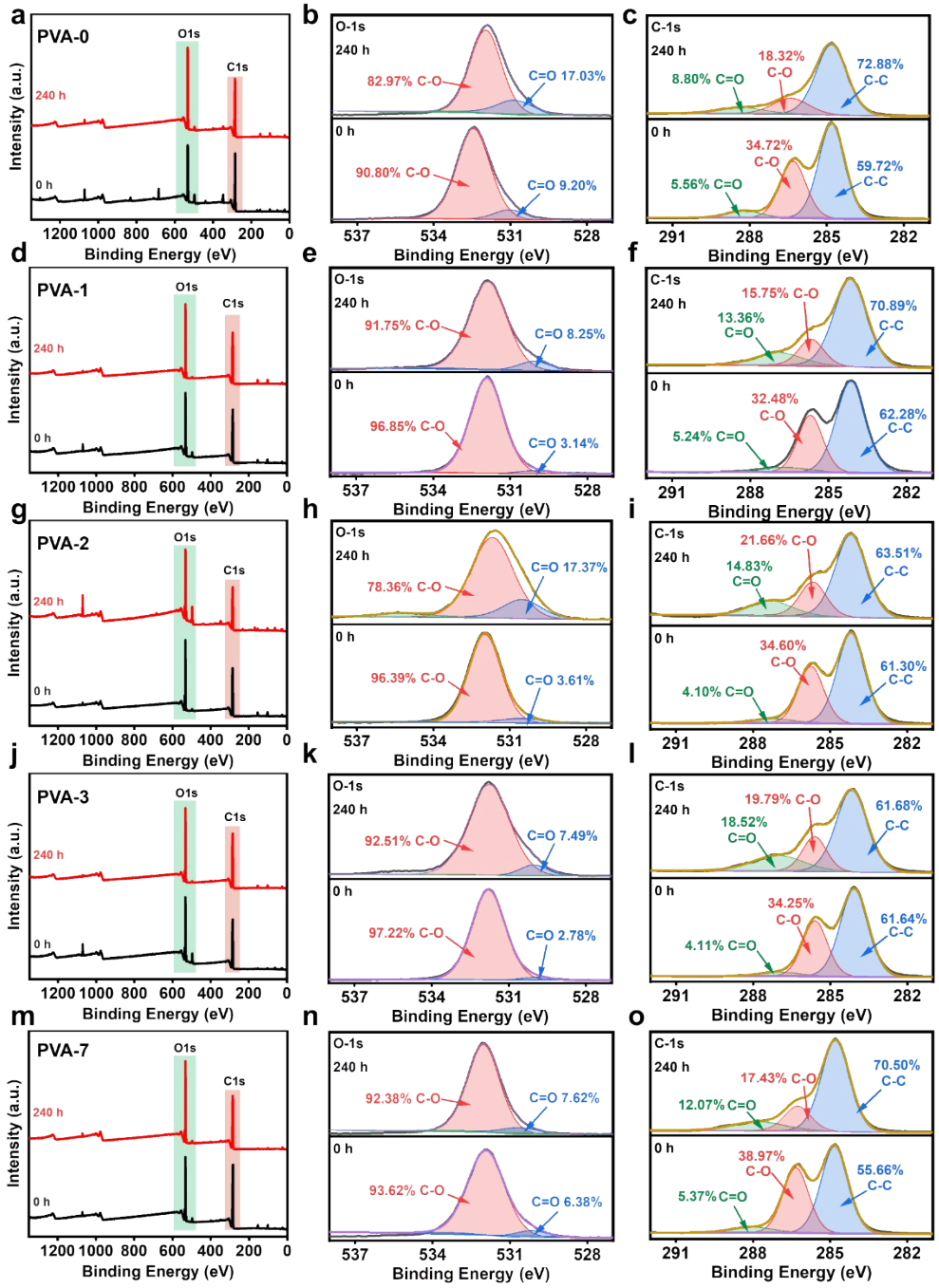


Figure S27 a) XPS spectra, b) O 1s, c) C 1s high resolution spectra of PVA-0 before and after photoaging for 240 h. d) XPS spectra, e) O 1s, f) C 1s high resolution spectra of PVA-1 before and after photoaging for 240 h. g) XPS spectra, h) O 1s, i) C 1s high resolution spectra of PVA-2 before and after photoaging for 240 h. j) XPS spectra, k) O 1s, l) C 1s high resolution spectra of PVA-3 before and after photoaging for 240 h. m) XPS spectra, n) O 1s, o) C 1s high resolution spectra of PVA-0 before and after photoaging for 240 h.

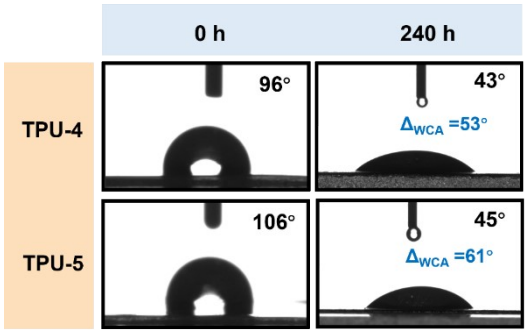


Figure S28 Water contact angles of TPU-4 and TPU-5 films before and after photoaging for 240 h.

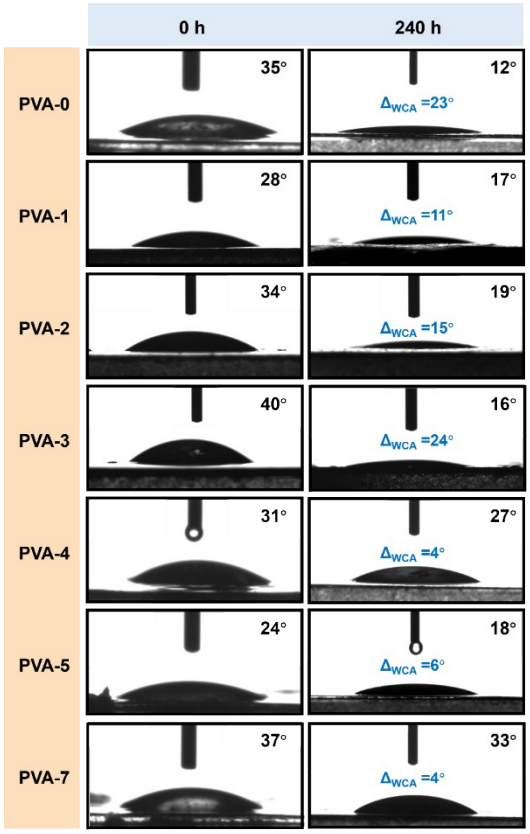


Figure S29 Water contact angles of PVA-0 and different PVA-based composite films before and after photoaging for 240 h.

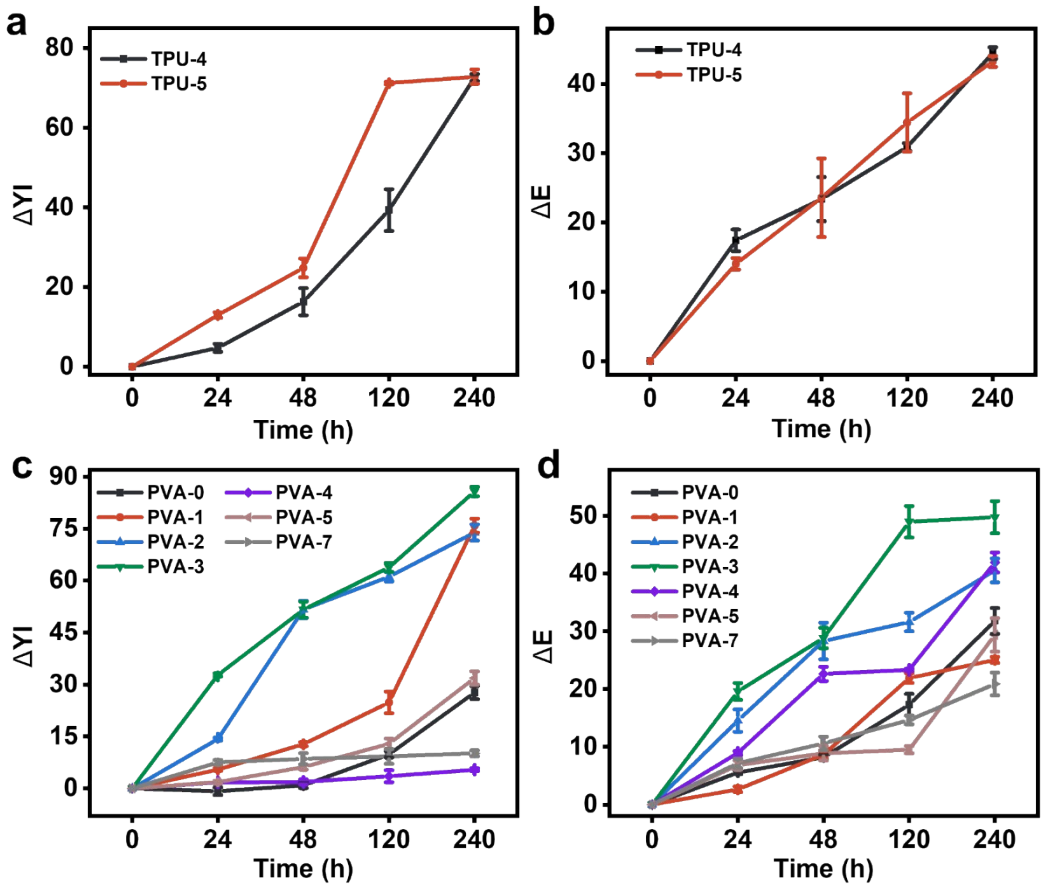


Figure S30 Changes in a) Yellowness index (ΔYI) and b) Total color difference (ΔE) of TPU-4 and different TPU-5 films during photoaging. Changes in a) ΔYI and b) ΔE of PVA-0 and different PVA-based composite films during photoaging.

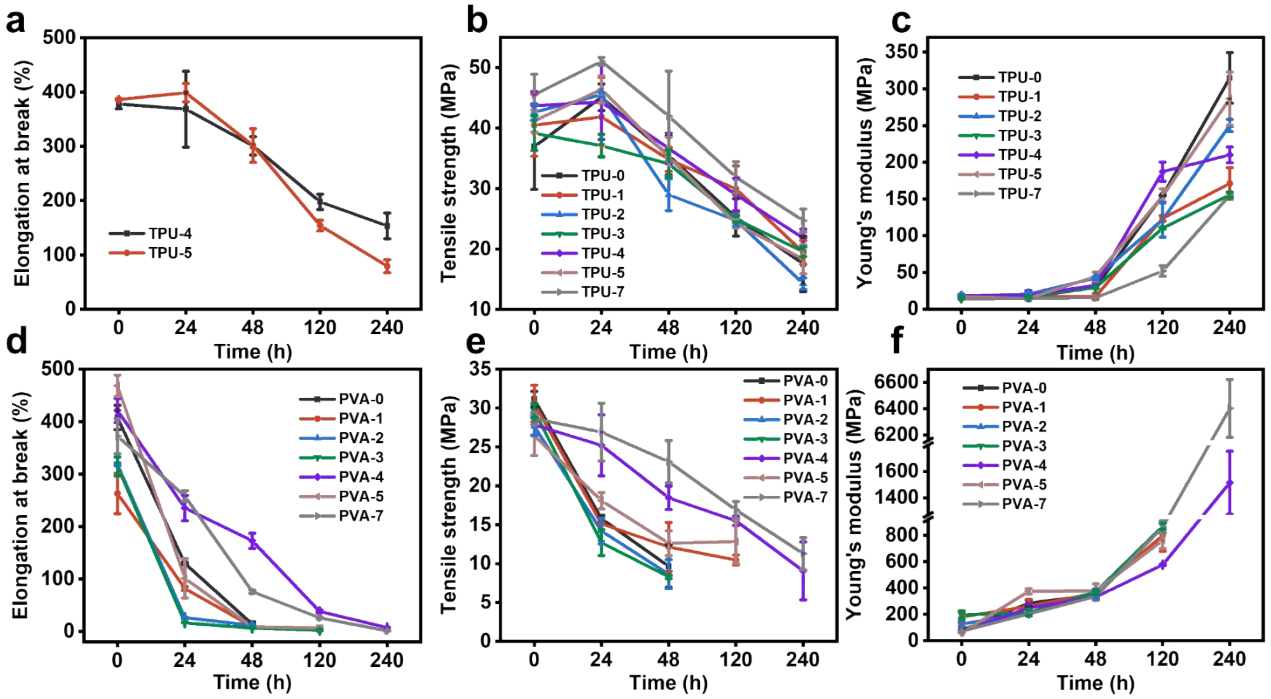


Figure S31 Changes in a) Elongation at break in TPU-4 and TPU-5 composite films during photoaging. Changes in b) Tensile strength and c) Young's modulus of TPU-0 and different TPU-based composite films during photoaging. Changes in d) Elongation at break, e) Tensile strength and f) Young's modulus of PVA-0 and different PVA-based composite films during photoaging.

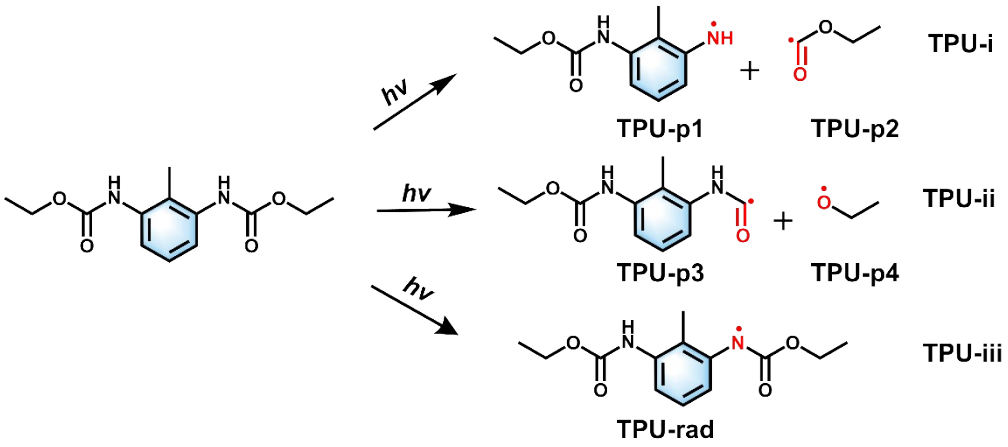


Figure S32 Possible reactions TPU under UV condition.

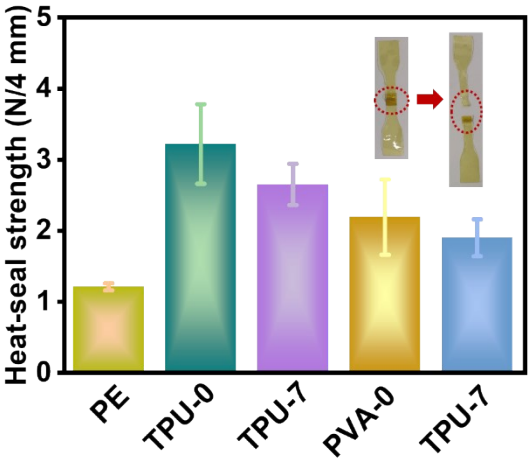


Figure S33 heat-seal strength properties of different films.

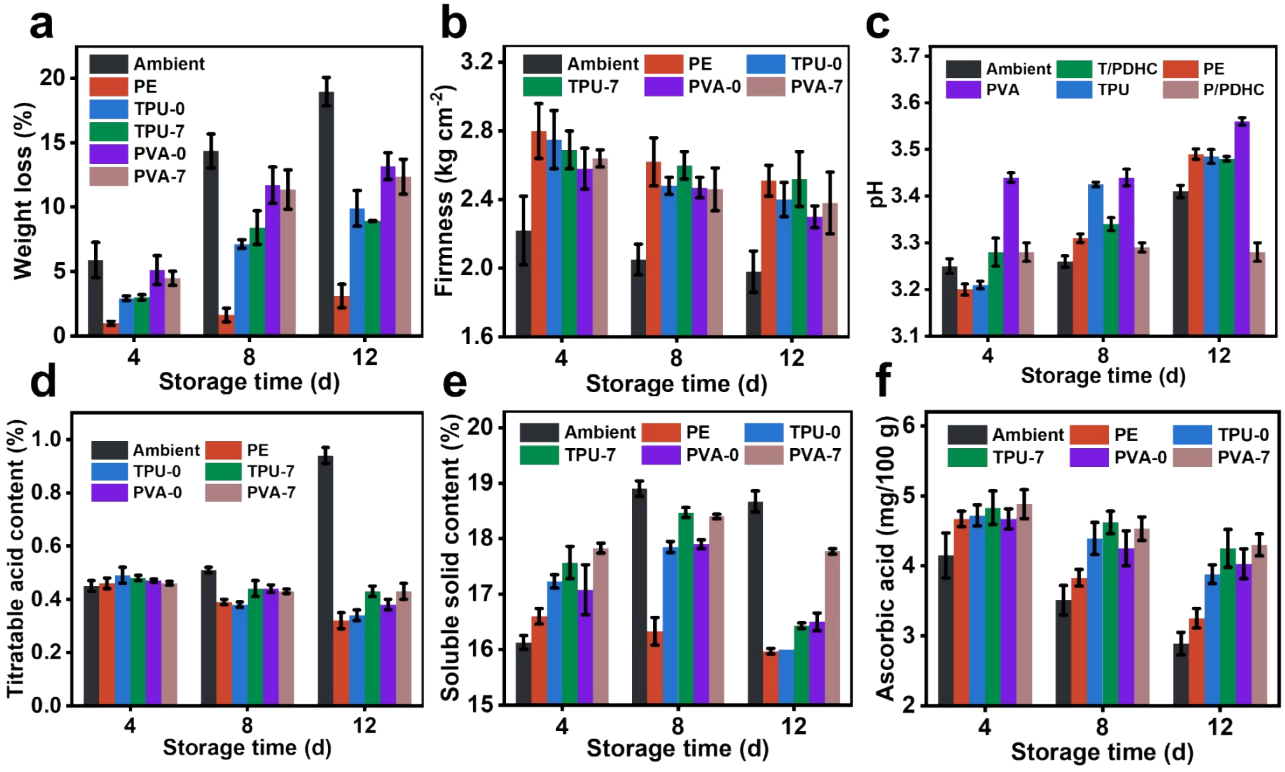


Figure S34 The changes of a) weight loss, b) firmness, c) pH, d) titratable acid content, e) soluble solid content and f) ascorbic acid content of *Kyoho* grapes during storage times.

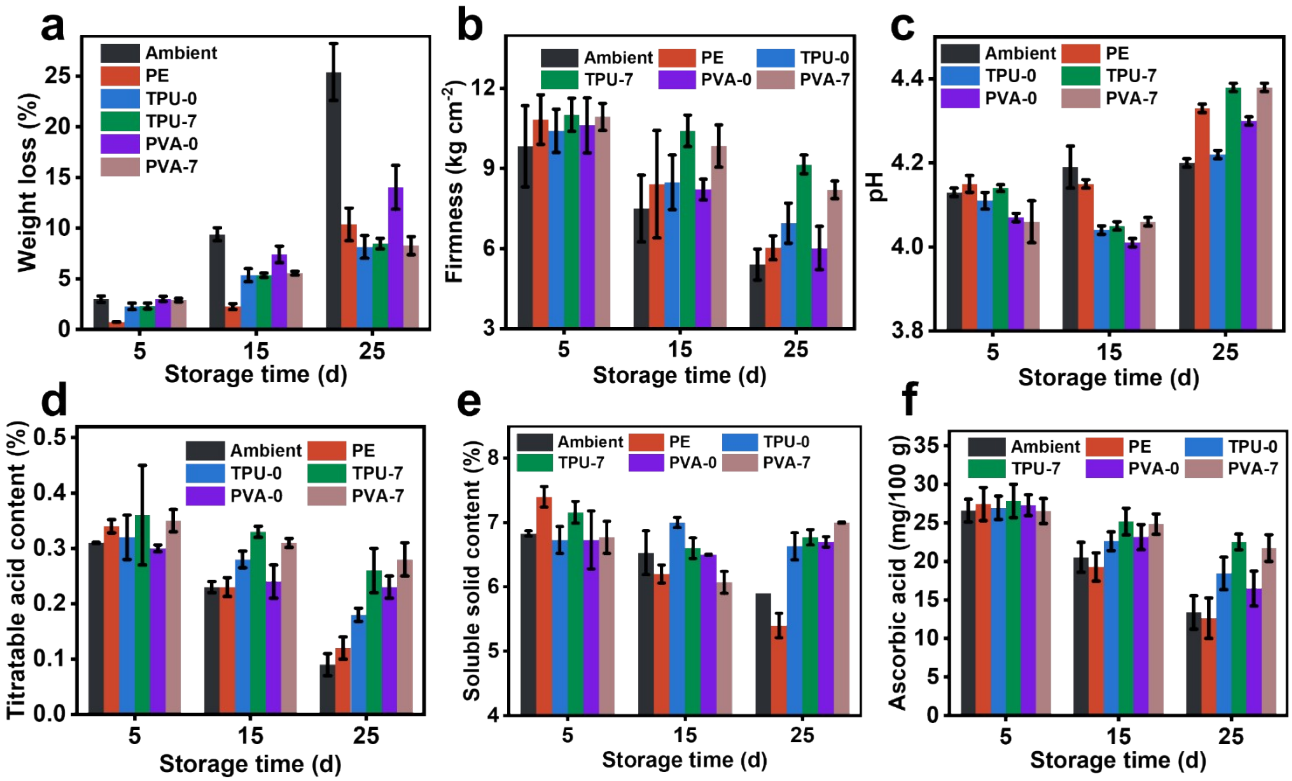


Figure S35 The changes of a) weight loss, b) firmness, c) pH, d) titratable acid content, e) soluble solid content and f) ascorbic acid content of *Millennium* cherry tomatoes during storage times.

Table S1 Experimental conditions of NP-1 and NP-2 fabrication.

Sample	HC or MU (mg)	HRP (10 mg/mL, μL)	H_2O_2 (10 mg/mL, μL)	RO Water (mL)	Acetonitrile (mL)	Time (h)
NP-1-1	90	100	1300	18	12	6
NP-1-2	90	300	3900	18	12	6
NP-1-3	90	600	7800	18	12	6
NP-1-4	90	800	10400	18	12	6
NP-1-5	90	1000	13000	18	12	6
NP-2-1	90	100	1300	18	12	6
NP-2-2	90	300	3900	18	12	6
NP-2-3	90	600	7800	18	12	6
NP-2-4	90	800	10400	18	12	6
NP-2-5	90	1000	13000	18	12	6

Table S2 Experimental conditions of NP-3 fabrication.

Sample	DHC (mg)	HRP (10 mg/mL, μL)	H_2O_2 (10 mg/mL, μL)	RO Water (mL)	Methanol (mL)	Time (h)
NP-3-1	90	100	2500	15	15	6
NP-3-2	90	300	7500	15	15	6
NP-3-3	90	600	15000	15	15	6
NP-3-4	90	800	20000	15	15	6
NP-3-5	90	1000	25000	15	15	6

Table S3 Summary of physical parameters of NP-1, NP-2 and NP-3.

Sample	$Size_{SEM}$ (nm)	$Size_{DLS}$ (nm)	PDI	Zeta (mV)	Yield (%)
NP-1-1	83±6	99	0.051	-19.2	13.05±2.41
NP-1-2	100±7	118	0.104	-18.8	35.89±5.24
NP-1-3	142±19	204	0.152	-18.3	92.73±4.10
NP-1-4	145±1	228	0.117	-16.8	93.52±3.69
NP-1-5	156±10	255	0.136	-21.8	95.28±2.73
NP-2-1	221±10	317	0.216	-16.9	17.29±1.74
NP-2-2	173±7	259	0.172	-17.8	90.22±3.75
NP-2-3	142±17	202	0.106	-16.3	91.67±3.59
NP-2-4	107±7	150	0.095	-21.6	95.61±1.03
NP-2-5	98±6	136	0.208	-20.4	97.52±1.52
NP-3-1	113±9	150	0.103	-20.2	9.60±1.59
NP-3-2	123±7	173	0.075	-16.7	35.40±3.52
NP-3-3	136±19	188	0.124	-23.1	63.57±4.60
NP-3-4	147±10	196	0.214	-19.6	68.47±3.93
NP-3-5	155±13	184	0.202	-21.6	70.33±3.56

Table S4 TGA data for UV326, coumarin monomers and poly(coumarin) NPs under N_2.

Sample	T_{max} (℃)	C_{800} (%)
UV326	337.64	0.77
AO1010	410.33	4.21
HC	289.18	0.80
MU	302.21	0.00
DHC	337.64	18.80
NP-1	369.72	37.88
NP-2	355.71	41.40
NP-3	417.10	38.24

T_{max}: Temperature at maximum thermal degradation rate; C_{800}: Char yield at 800 ℃

Table S5 Compositions of the solution used in TPU-based composite films preparation.

Sample	UV326 (mg)	AO1010 (mg)	NP-1 (mg)	NP-2 (mg)	NP-3 (mg)
TPU-0	0	0	0	0	0
TPU-1	60 (1%)	0	0	0	0
TPU-2	0	60 (1%)	0	0	0
TPU-3	60 (1%)	60 (1%)	0	0	0
TPU-4	0	0	60 (1%)	0	0
TPU-5	0	0	0	60 (1%)	0
TPU-6	0	0	0	0	30 (0.5%)
TPU-7	0	0	0	0	60 (1%)
TPU-8	0	0	0	0	120 (2%)

Table S6 Compositions of the solution used in PVA-based composite films preparation.

Sample	UV326 (mg)	AO1010 (mg)	NP-1 (mg)	NP-2 (mg)	NP-3 (mg)
PVA-0	0	0	0	0	0
PVA-1	60 (1%)	0	0	0	0
PVA-2	0	60 (1%)	0	0	0
PVA-3	60 (1%)	60 (1%)	0	0	0
PVA-4	0	0	60 (1%)	0	0
PVA-5	0	0	0	60 (1%)	0
PVA-6	0	0	0	0	30 (0.5%)
PVA-7	0	0	0	0	60 (1%)
PVA-8	0	0	0	0	120 (2%)

Table S7 The UPF, UVB shielding efficiency, UVA shielding efficiency, UV shielding at 400 nm and transparency of different films.

Samples	UPF	UVB shielding efficiency (%)	UVA shielding efficiency (%)	UV shielding at 400 nm (%)	Transparency T_{660} (%)
TPU-0	2.21	16.36	29.62	17.63	87.81
TPU-1	44.7	99.42	91.72	42.42	90.43
TPU-2	2.28	89.65	37.83	20.48	90.31
TPU-3	45.44	99.38	92.42	44.64	88.48
TPU-4	89.61	99.73	95.44	83.78	74.23
TPU-5	63.63	99.97	92.64	70.11	78.85
TPU-6	13.67	97.07	88.50	68.61	78.67
TPU-7	91.40	99.64	98.27	92.01	64.07
TPU-8	410.39	99.91	99.42	96.33	53.11
PVA-0	1.26	21.89	15.38	11.81	91.40
PVA-1	1.47	32.98	29.21	27.17	76.57
PVA-2	1.19	20.74	14.63	12.33	89.15
PVA-3	1.37	30.49	27.50	24.25	82.27
PVA-4	63.63	99.18	98.39	91.77	88.58
PVA-5	22.34	94.33	95.77	88.64	89.80
PVA-6	5.35	78.94	88.98	89.30	91.05
PVA-7	74.66	96.46	99.04	98.76	88.07
PVA-8	629.86	99.83	99.97	99.97	84.64

Table S8 Tensile strength, elongation at break and Young's modulus of neat TPU and different TPU-based composite films.

Sample	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
TPU-0	36.93±7.07	365.38±11.35	14.52±0.66
TPU-1	40.49±5.15	385.70±7.70	18.17±0.64
TPU-2	42.62±1.29	388.83±24.24	17.59±0.97
TPU-3	39.15±2.87	374.34±9.24	15.46±0.86
TPU-4	43.71±2.35	378.04±8.96	17.94±2.29
TPU-5	41.18±1.80	386.23±1.82	16.50±0.89
TPU-6	42.01±2.97	391.98±22.61	17.39±0.65
TPU-7	45.51±3.42	448.00±31.47	13.96±0.25
TPU-8	48.86±4.03	429.09±13.20	16.07±0.92

Table S9 Tensile strength, elongation at break and Young's modulus of neat PVA and different PVA-based composite films.

Sample	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
PVA-0	31.16±1.00	375.32±12.91	79.01±4.09
PVA-1	30.60±2.34	263.29±38.52	188.88±48.28
PVA-2	27.68±1.15	318.79±2.58	125.22±17.29
PVA-3	29.65±0.91	314.57±18.08	194.92±30.47
PVA-4	27.85±1.39	395.56±21.84	67.60±5.68
PVA-5	26.46±2.57	381.42±25.94	59.80±3.21
PVA-6	24.84±1.54	228.95±26.53	67.11±2.52
PVA-7	28.64±0.78	405.01±8.86	71.12±3.50
PVA-8	26.58±2.66	327.84±36.55	86.82±7.95

Table S10 TGA data for neat TPU and different TPU-based composite films under N_2.

Sample	T_{max} (°C)	C_{800} (%)
TPU-0	360.15	4.06
TPU-1	356.99	5.38
TPU-2	343.67	5.30
TPU-3	341.00	5.96
TPU-4	360.15	4.28
TPU-5	361.73	5.71
TPU-6	368.58	4.32
TPU-7	367.52	5.09
TPU-8	362.25	5.67

Table S11 TGA data for neat PVA and different PVA-based composite films under N_2.

Sample	T_{max} (℃)	C_{800} (%)
PVA-0	274.25	6.26
PVA-1	267.36	7.01
PVA-2	257.17	12.24
PVA-3	256.83	8.30
PVA-4	275.30	6.50
PVA-5	304.99	8.19
PVA-6	272.84	6.32
PVA-7	275.30	5.70
PVA-8	278.99	4.89

Table S12 Surface elemental composition of TPU and T/PDHC-1 obtained from XPS analysis.

Sample	Irradiation time (h)	Atomic percentage (%)			Atomic ratio
		C 1s	O 1s	N 1s	C1s/O1s
TPU-0	0	72.12	24.07	3.82	3.00
	240	57.75	33.59	8.65	1.72
TPU-1	0	71.78	24.26	3.96	2.96
	240	61.51	32.89	5.6	1.87
TPU-2	0	72.76	23.43	3.82	3.11
	240	63.43	31.56	5.01	2.01
TPU-3	0	73.91	22.04	4.05	3.35
	240	55.68	35.31	9.01	1.58
TPU-7	0	72.72	23.41	3.87	3.11
	240	66.24	26.63	7.13	2.49

Table S13 Surface elemental composition of PVA and P/PDHC-1 obtained from XPS analysis.

Sample	Irradiation time (h)	Atomic percentage (%)		Atomic ratio
		C 1s	O 1s	C1s/O1s
PVA-0	0	70.97	29.03	2.44
	240	68.19	31.71	2.15
PVA-1	0	69.77	30.23	2.31
	240	68.65	31.35	2.19
PVA-2	0	69.04	30.96	2.23
	240	60.93	39.07	1.56
PVA-3	0	69.72	30.28	2.30
	240	68.52	31.48	2.18
PVA-7	0	72.79	27.21	2.68
	240	70.25	29.75	2.36

Table S14 The energies of different structures for TPU, UV326, NP and AO1010.

Species	E (Hartree)	G_{corr} (Hartree)	G_{total} (Hartree)
H-rad	-0.5021559	-0.0106541	-0.512810
TPU	-917.0148379	0.253932	-916.760906
TPU-rad	-916.3590768	0.239788	-916.119289
TPU-p1	-649.06497	0.177447	-648.887523
TPU-p2	-267.8120134	0.047905	-267.764108
TPU-p3	-762.4346904	0.184975	-762.249715
TPU-p4	-154.426584	0.038868	-154.387716
UV326	-1358.6799051	0.275512	-1358.404393
UV326-rad	-1358.0257409	0.260542	-1357.765199
NP	-1294.1898365	0.201997	-1293.987840
NP-rad1	-1293.5619172	0.189697	-1293.372220
NP-rad2	-1293.5642428	0.190032	-1293.374211
EtOOH	-230.255363	0.055617	-230.199746
EtOO-rad	-229.616307	0.043370	-229.572936
AO1010	-968.174700	0.402315	-967.772384
TS1	-1523.811806	0.258251	-1523.553555
TS2	-1197.790746	0.458548	-1197.332198
TS3	-1146.617375	0.310308	-1146.307067

Table S15 The free energies of dissociation for different bond in TPU, NP and UV326.

	ΔG (Hartree)	ΔG (kJ/mol)
TPU-i=TPU-rad+H-rad	0.128806	338.181
TPU-ii= TPU-p1+ TPU-p2	0.109275	286.900
TPUiii= TPU-p3+ TPU-p4	0.123475	324.183
NPi=NP-rad1+H-rad	0.102809	269.926
NPii=NP-rad2+H-rad	0.100819	264.700
UV326= UV326-rad+H-rad	0.126384	331.821

Table S16 Reaction energy barriers of NP, AO1010 and TPU with peroxyl radicals (EtOO-rad).

Energy barrier of reactions	ΔG (Hartree)	ΔG (kJ/mol)
$E_{barrier-NP}$=TS1-NP-EtOO-rad	0.007221	18.959
$E_{barrier-AO1010}$=TS2-AO1010-EtOO-rad	0.013123	34.455
$E_{barrier-TPU}$= TS3-TPU-H-EtOO-rad	0.026775	70.297

Molecular structure XYZ Coordinates

H-rad

H	-0.41228100	-0.47368400	0.00000000

TPU

C	-3.11863400	0.50283200	1.47778100
C	-1.79119100	0.61709600	1.87456200
C	-0.91640300	1.41352100	1.12917400
C	-1.36243300	2.09620000	-0.02042500
C	-2.72518400	2.00001100	-0.36724700
C	-3.60015000	1.20367800	0.37796200
H	-3.79811200	-0.11404400	2.05733000
H	-1.42698000	0.09972800	2.75063700

H	-4.64045600	1.14172600	0.09201100
C	-0.40218600	2.89325400	-0.86890800
H	-0.32331100	3.94317000	-0.55283800
H	0.60231900	2.46498100	-0.82992300
H	-0.71180900	2.89091200	-1.91680700
N	0.43008100	1.59324800	1.52596700
H	0.86300200	2.48273400	1.33032100
C	1.32956200	0.71174500	2.07980500
O	2.47366200	1.02701700	2.35196500
O	0.80573800	-0.51684600	2.27102100
C	1.72018000	-1.48900500	2.82351600
H	2.56454300	-1.60868300	2.13827200
H	2.11434900	-1.10802900	3.76986800
C	0.94394700	-2.77762100	3.00198400
H	0.54374100	-3.12619200	2.04607300
H	1.60100300	-3.55330400	3.40633600
H	0.10918200	-2.63806300	3.69466000
N	-3.18522900	2.76545100	-1.46511200
H	-2.73391000	3.64930800	-1.64399700
C	-4.12235900	2.47919700	-2.43083800
O	-4.39510800	3.25378700	-3.32975700
O	-4.68161700	1.26185300	-2.27040000
C	-5.65202100	0.90047000	-3.27749300
H	-6.43570500	1.66280400	-3.30525900
H	-5.16106400	0.89570000	-4.25513500
C	-6.19198200	-0.46484700	-2.90429100
H	-6.68377100	-0.43686400	-1.92783400
H	-6.92395300	-0.79043700	-3.64935300
H	-5.38699900	-1.20360900	-2.86347200

TPU-rad

C	1.44545600	1.22543700	1.85747000
C	0.20243000	1.40596200	1.29303300
C	-0.13755000	0.72533600	0.07858400
C	0.83955600	-0.13154600	-0.54522200
C	2.09087900	-0.28709200	0.06147000
C	2.39052300	0.37797500	1.26517600
H	1.70000900	1.73198000	2.78287200
H	-0.54225300	2.03282300	1.76509700
H	3.35553700	0.22990800	1.72661800
C	0.50598500	-0.84152600	-1.82701200
H	0.44475500	-1.92898200	-1.68106600
H	-0.45940000	-0.50344700	-2.19932800
H	1.26813900	-0.65456800	-2.59226200

C	-2.35825400	1.56677300	0.02746900
O	-2.79641800	1.40022600	1.15396300
O	-2.90676300	2.40248200	-0.87721900
C	-4.06103100	3.13647900	-0.41485000
H	-4.84235200	2.42421900	-0.13218600
H	-3.79073400	3.69934200	0.48426300
C	-4.49817000	4.04428900	-1.54643300
H	-4.75836100	3.46108900	-2.43391100
H	-5.37603600	4.62199300	-1.24179700
H	-3.70074500	4.74249000	-1.81539400
N	3.00452100	-1.17168300	-0.54623000
H	2.62327600	-1.84365700	-1.19484900
C	4.38194400	-1.21176700	-0.55174300
O	5.00512400	-2.03628600	-1.19303200
O	4.94179800	-0.25075700	0.21157700
C	6.38851900	-0.23980600	0.21318500
H	6.74830000	-1.21882400	0.54122000
H	6.73880700	-0.08349400	-0.81097600
C	6.82403800	0.87426200	1.14229200
H	6.47084100	0.69465900	2.16176100
H	7.91620800	0.93240000	1.16306400
H	6.43317800	1.83812200	0.80506000
N	-1.30875600	0.87125900	-0.55568700

TPU-p1

C	-0.02617300	1.19948300	-1.61197800
C	1.17668000	0.62401300	-1.26091000
C	1.22135300	-0.62175500	-0.55344600
C	-0.02921700	-1.24474400	-0.17275700
C	-1.22628600	-0.64738600	-0.57272300
C	-1.23033400	0.56318300	-1.29435500
H	-0.04766200	2.13723400	-2.15784000
H	2.12902300	1.07649200	-1.51231100
H	-2.17638100	0.99209600	-1.59400500
C	-0.03209400	-2.51559100	0.63446700
H	-0.01139800	-3.41321800	0.00168000
H	0.83557900	-2.57035800	1.29668800
H	-0.92038500	-2.57593500	1.26808300
N	2.43872200	-1.10949200	-0.29848100
H	2.36424800	-2.00329500	0.19595400
N	-2.44571900	-1.31113800	-0.29458600
H	-2.44378200	-2.31959600	-0.28963700
C	-3.65972300	-0.80583100	0.11350600
O	-4.61953900	-1.51417200	0.35308500

O	-3.65029200	0.53944800	0.21824200
C	-4.89339900	1.12510600	0.66642400
H	-5.69392700	0.82066600	-0.01363700
H	-5.13227200	0.72828100	1.65738800
C	-4.69563800	2.62677100	0.68555000
H	-4.46293700	3.00328600	-0.31454900
H	-5.61005500	3.11632300	1.03333900
H	-3.87813900	2.90317300	1.35688300

TPU-p2

C	3.66640800	-0.78072900	0.14272400
O	4.51906000	-1.58056800	0.40011500
O	3.68965600	0.53640600	0.19956600
C	4.95905900	1.13810900	0.64946900
H	5.17856300	0.74463000	1.64566600
H	5.74462700	0.80724200	-0.03524100
C	4.77192000	2.63743500	0.64229200
H	3.96564700	2.93264300	1.31875600
H	5.69492300	3.12495200	0.97137100
H	4.53190500	2.99528400	-0.36228000

TPU-p3

C	0.02603400	1.18988300	-1.51464900
C	1.22296500	0.57414900	-1.16948000
C	1.19351600	-0.64603800	-0.49011100
C	-0.02176200	-1.25704400	-0.13357200
C	-1.21818700	-0.62902500	-0.53820700
C	-1.19400900	0.58902500	-1.22486300
H	0.04456900	2.13576600	-2.04617200
H	2.17854000	1.01884800	-1.42149000
H	-2.12435600	1.05044400	-1.52367200
C	-0.04485200	-2.53207100	0.67492500
H	0.04348600	-3.43343300	0.05321900
H	0.76910400	-2.55554800	1.40575100
H	-0.97235300	-2.61555700	1.24522400
N	2.40812500	-1.28441800	-0.14407400
H	2.37699100	-2.26105800	0.13206100
C	3.62584200	-0.70037800	-0.19877600
O	4.69532700	-1.18975500	0.04844300
N	-2.43933300	-1.28958000	-0.26837500
H	-2.44778200	-2.29766700	-0.29318700
C	-3.66815600	-0.78749300	0.09812300
O	-4.63320700	-1.50167700	0.29783900
O	-3.66650000	0.55552800	0.21683500

C	-4.92543600	1.13233600	0.63092100
H	-5.70349000	0.82861200	-0.07501400
H	-5.19239000	0.72794000	1.61166900
C	-4.73552300	2.63472200	0.66571700
H	-4.47473600	3.01870900	-0.32452800
H	-5.66227200	3.11774500	0.98919100
H	-3.93966800	2.91037600	1.36285300

TPU-p4

O	3.74128500	0.47023200	0.21647000
C	4.86584100	1.12592100	0.64363800
H	5.15777300	0.73106700	1.63727800
H	5.68693500	0.77515700	-0.01766200
C	4.77698500	2.65052000	0.64170500
H	3.98580500	2.98610500	1.31843600
H	5.72149600	3.09842200	0.96810000
H	4.54541400	3.01768300	-0.36205500

UV326

C	-4.99050900	0.15768800	0.43786200
C	-3.77038400	0.20013100	-0.21880500
C	-3.18735400	1.43135600	-0.53123200
C	-3.81124200	2.65566400	-0.19398100
C	-5.05873900	2.62349700	0.47756000
C	-5.60483700	1.37399300	0.76995200
H	-3.24778900	-0.70509200	-0.50118400
H	-6.55726200	1.32770600	1.28244200
C	-0.17086600	2.11967200	-2.15428600
C	-0.19142100	0.69570200	-2.14567300
C	0.90133100	2.83140000	-2.73050900
C	0.85859400	-0.05703100	-2.71239700
C	1.92366100	2.09093500	-3.28230300
H	0.91876000	3.91494000	-2.73808900
C	1.89043300	0.66687700	-3.26680500
H	0.85014000	-1.13932300	-2.70967000
H	2.77387500	2.58285600	-3.73935600
O	-3.25887900	3.85182300	-0.49011500
H	-2.40017400	3.69207400	-0.95235800
N	-1.29799000	2.54948900	-1.54675600
N	-1.32496200	0.28125000	-1.53583500
N	-1.93288900	1.41752900	-1.20662200
Cl	3.24181700	-0.18530000	-3.99596500
C	-5.63579000	-1.16226900	0.78364600
H	-5.82944600	-1.76035300	-0.11356500

H	-4.99469000	-1.76164700	1.43934600
H	-6.58943100	-1.01276700	1.29640300
C	-5.77737600	3.92810600	0.86568900
C	-4.89277300	4.75090300	1.83007800
H	-3.94194100	5.02025800	1.37142500
H	-5.41330100	5.67155100	2.11550300
H	-4.68960000	4.18122200	2.74286300
C	-6.09427900	4.75308700	-0.40257400
H	-6.61887600	5.67353700	-0.12400000
H	-5.18744800	5.02288500	-0.94283200
H	-6.74425700	4.18479600	-1.07603400
C	-7.11110900	3.65346400	1.58323200
H	-7.81141700	3.09830900	0.95108600
H	-6.96959300	3.09770500	2.51560700
H	-7.58201300	4.60768600	1.83698800

UV326-rad

C	-2.49369400	2.31768500	-0.12873300
C	-1.14443900	1.92063800	-0.10677500
C	-0.82136400	0.58727400	-0.01599000
C	-1.84342000	-0.45712800	0.12766600
C	-3.24574900	-0.01751900	0.03862900
C	-3.50572100	1.33491200	-0.07175000
H	-0.34865100	2.65419500	-0.16824900
H	-4.53160400	1.67952200	-0.11715600
C	2.31795000	-0.81591100	-0.40206200
C	2.61020800	0.38057100	0.32528000
C	3.35099100	-1.69812000	-0.79709000
C	3.93634600	0.71906500	0.68169400
C	4.63682400	-1.36001300	-0.45065100
H	3.12915000	-2.60454700	-1.34807200
C	4.91077900	-0.16282500	0.28058100
H	4.16701600	1.61961300	1.23614300
H	5.46894800	-1.99765600	-0.72413900
O	-1.52153600	-1.64048100	0.35921400
N	0.98939100	-0.88662700	-0.60158100
N	1.45579500	1.02911400	0.56503000
N	0.54186100	0.22051100	-0.00220900
Cl	6.58959200	0.17495300	0.67423500
C	-2.84051900	3.77538400	-0.23868500
H	-2.42184100	4.34061100	0.60202000
H	-2.42102400	4.21078100	-1.15313100
H	-3.92112100	3.93234000	-0.25141200
C	-4.35835900	-1.06410900	0.10420200

C	-4.16123000	-2.10065900	-1.02734800
H	-3.20773500	-2.61766500	-0.92488200
H	-4.96782100	-2.84021000	-0.98954600
H	-4.19498600	-1.61460800	-2.00806800
C	-4.31974200	-1.77522600	1.47848500
H	-5.13139900	-2.50848500	1.53279600
H	-3.37057500	-2.28899300	1.62562300
H	-4.46070300	-1.05452400	2.29078400
C	-5.75019200	-0.43174100	-0.06668800
H	-5.98209400	0.27658900	0.73523600
H	-5.85071100	0.08486800	-1.02680700
H	-6.50706500	-1.22051700	-0.03522100

NP

C	-4.17874600	0.62105800	-2.70405500
C	-3.15943200	0.36500900	-1.85238500
C	-2.75071300	1.33535000	-0.87381200
C	-3.46459800	2.54365500	-0.84255200
C	-4.90939400	1.87846600	-2.67179400
H	-4.50535900	-0.09169300	-3.45065700
H	-2.63790100	-0.58492500	-1.89292200
C	-1.69285000	1.13390500	0.04940900
C	-3.16099200	3.54663000	0.07934500
C	-2.12715900	3.33266500	0.97470700
C	-1.38588500	2.13107500	0.96630600
H	-3.73508800	4.46726000	0.07477800
C	-0.89688500	-0.11875000	0.04801000
C	-0.03735800	-0.44253300	-1.01452300
C	-0.96158300	-1.00625100	1.12438200
C	0.73603100	-1.61613500	-1.02019700
C	-0.18403000	-2.18768800	1.13654300
C	0.81861100	0.24368100	-3.18327700
C	1.57714300	-1.85041600	-2.15959300
C	0.65015800	-2.49005300	0.08249500
C	1.61869600	-0.97191000	-3.18814700
H	2.18351600	-2.75225600	-2.18152500
H	1.24400400	-3.40036600	0.09073200
H	2.24151700	-1.12165800	-4.06084000
O	-1.72950800	4.23717400	1.92348500
H	-2.25037700	5.04661500	1.84888500
O	-0.36318300	1.96321600	1.84818000
H	-0.31388200	2.76381300	2.39159800
O	-1.78677700	-0.74294700	2.16082600
H	-1.67574400	-1.45296800	2.81233000

O	-0.35765000	-2.96166800	2.25985100
H	0.22115300	-3.73293800	2.22547400
O	0.01433500	0.43784300	-2.05339200
O	-4.49239500	2.79538600	-1.70208800
O	0.78247300	1.08626700	-4.04721100
O	-5.83136000	2.19665900	-3.38561800

NP-rad1

C	-2.23746900	1.93284900	-1.70356300
C	-1.22279900	1.15067700	-1.25674400
C	-1.46898900	0.05870600	-0.36990300
C	-2.83857400	-0.18781400	0.00585100
C	-3.61998000	1.69743400	-1.30703700
H	-2.07732800	2.76717100	-2.37461000
H	-0.20437500	1.34171800	-1.57367400
C	-0.43768200	-0.77610200	0.12533000
C	-3.20688600	-1.22324100	0.82177100
C	-2.19754000	-2.09802000	1.33623600
C	-0.79433900	-1.82510700	0.95746100
H	-4.24454200	-1.38580700	1.08356200
C	0.98999600	-0.54888800	-0.20729600
C	1.67545400	0.59848000	0.22627200
C	1.71099400	-1.50430400	-0.92788500
C	3.03894800	0.80079300	-0.04494500
C	3.08578600	-1.31775300	-1.20264800
C	1.49878900	2.71736000	1.40680900
C	3.63943800	2.01013400	0.44405600
C	3.73979800	-0.18464800	-0.76970400
C	2.91330800	2.92072300	1.13316700
H	4.69461700	2.18231900	0.24879500
H	4.79538100	-0.04022100	-0.98418200
H	3.33778200	3.84172500	1.51188400
O	-2.38866200	-3.07888500	2.09013900
O	0.08997700	-2.66035100	1.49152800
H	-0.47314000	-3.27723000	2.02011500
O	1.08521800	-2.61266800	-1.37770000
H	1.74730800	-3.16971000	-1.81660300
O	3.65568100	-2.34065700	-1.92094400
H	4.60106700	-2.18429000	-2.03518800
O	0.95319200	1.51798700	0.92529500
O	-3.83880600	0.61774900	-0.45905800
O	0.76025800	3.46804000	1.99583200
O	-4.57569200	2.34705400	-1.65712300

NP-rad2

C	-2.26677100	1.97627900	-1.67381300
C	-1.24603400	1.19835300	-1.25277000
C	-1.46839900	0.08387800	-0.36812100
C	-2.82096800	-0.17060900	0.01848100
C	-3.63770400	1.72652500	-1.26081800
H	-2.12286300	2.81916600	-2.33758700
H	-0.23353400	1.39723500	-1.58350800
C	-0.45070500	-0.74837200	0.10181100
C	-3.19164400	-1.23474200	0.84633500
C	-2.19400700	-2.06497200	1.30899900
C	-0.77909200	-1.85421800	0.96606700
H	-4.23143900	-1.38441800	1.10786500
C	0.97549100	-0.53119400	-0.22138400
C	1.66543900	0.61947800	0.19849500
C	1.70133000	-1.51233000	-0.90359300
C	3.03780900	0.79686500	-0.04414000
C	3.08384300	-1.34862300	-1.15096600
C	1.49432800	2.76439600	1.33350000
C	3.64414300	2.00779800	0.43266000
C	3.74242000	-0.21432200	-0.72864100
C	2.91660800	2.94315700	1.08646100
H	4.70584800	2.16072100	0.25767200
H	4.80412300	-0.08735300	-0.92302300
H	3.34609600	3.86582900	1.45529100
O	-2.42620500	-3.10457400	2.10362200
H	-1.52713200	-3.47704600	2.26585700
O	0.04965200	-2.65338300	1.47080200
O	1.06929100	-2.61332600	-1.35909900
H	1.73764100	-3.20149500	-1.74450500
O	3.65671500	-2.39247700	-1.83633000
H	4.61192000	-2.26925500	-1.89635900
O	0.94273100	1.56324200	0.86418200
O	-3.82842500	0.61781900	-0.41472900
O	0.75336100	3.53633600	1.89169000
O	-4.61727100	2.35520700	-1.57280900

EtOOH

C	-2.16353200	0.37987900	0.01947600
H	-1.79937300	-0.65063000	0.00054100
H	-1.80515000	0.89233400	-0.87795700
H	-3.25662400	0.36161000	-0.00553300
C	-1.66123400	1.10339100	1.25925000
H	-0.56484400	1.12053200	1.29505500

H	-2.02157600	2.14185500	1.28939700
O	-2.16648600	0.37768200	2.37676500
O	-1.62435800	1.01445300	3.56654100
H	-2.43167400	1.41825000	3.92522300

EtOO-rad

C	-2.16337000	0.37608300	0.01443100
H	-1.80829300	-0.65792700	0.00712800
H	-1.81602000	0.86508100	-0.90025700
H	-3.25660800	0.36814600	0.00568000
C	-1.63628400	1.12177100	1.22267300
H	-0.54376900	1.12401600	1.27635700
H	-1.99657600	2.15324500	1.27491900
O	-2.12859200	0.42850800	2.41036700
O	-1.70987000	1.02090700	3.51541300

AO1010

C	0.23516000	-0.05098600	-0.81119500
C	-0.47252900	-1.22317500	-0.55942500
C	-1.79232300	-1.21825200	-0.09367800
C	-2.39757400	0.04076000	0.11883700
C	-1.71833800	1.25628700	-0.12263800
C	-0.40423600	1.16855500	-0.58668100
H	0.02776800	-2.16675600	-0.73854500
H	0.14999300	2.07708100	-0.78811100
O	-3.69352500	0.15118700	0.57285500
H	-4.06628800	-0.72639300	0.69523800
C	-2.54087100	-2.54262600	0.16891400
C	-3.78054600	-2.66189700	-0.75376300
H	-4.31132100	-3.59867100	-0.55498500
H	-4.50302700	-1.84741600	-0.64946800
H	-3.46436200	-2.66252700	-1.80072400
C	-2.93652700	-2.65831000	1.66308600
H	-3.56591700	-1.84233100	2.02921700
H	-3.47604400	-3.59446200	1.84011800
H	-2.03711700	-2.65842700	2.28543500
C	-1.66230200	-3.77080900	-0.13607500
H	-1.35251100	-3.79884500	-1.18445400
H	-0.76628500	-3.79500300	0.49050100
H	-2.23345900	-4.68192900	0.06602900
C	-2.39318800	2.62146600	0.11082100
C	-2.79731600	2.76832400	1.59565800
H	-3.25842200	3.74852100	1.76053800
H	-3.50624700	1.99853100	1.89822600

H	-1.91435800	2.69839100	2.23962300
C	-3.63477100	2.76495700	-0.79866900
H	-4.37634000	1.99420600	-0.59182900
H	-4.09980500	3.74462300	-0.64183000
H	-3.34545700	2.69356500	-1.85233100
C	-1.44703800	3.79007800	-0.22139000
H	-0.54942900	3.78264100	0.40503100
H	-1.13657600	3.78179000	-1.27088400
H	-1.96837300	4.73459300	-0.03915400
C	1.67551700	-0.09656200	-1.26246300
H	1.87039300	-1.00955900	-1.83329900
H	1.89191400	0.73718600	-1.93794700
C	2.64424700	-0.03721000	-0.07499200
H	2.48955800	0.87562600	0.51180000
H	2.45781800	-0.86476900	0.62003300
C	4.09612000	-0.09308700	-0.49704700
O	4.91492200	0.00897800	0.57349400
C	6.33050900	-0.03862500	0.28556500
H	6.57812300	0.77226100	-0.40634300
H	6.55692900	-0.98153900	-0.22172500
C	7.06495800	0.09137000	1.60442600
H	6.79869600	-0.72563500	2.28078500
H	8.14533000	0.06036700	1.43399000
H	6.81999200	1.03748600	2.09500600
O	4.49499300	-0.21568500	-1.63581000

TS1-opt

C	0.73764200	3.24332200	-1.91216100
C	1.11244800	2.02426900	-1.45285500
C	0.14705000	1.09686000	-0.94699800
C	-1.21537400	1.50399000	-0.96883700
C	-0.65499800	3.66323800	-1.91975700
H	1.44802700	3.96371100	-2.29726100
H	2.15615000	1.73156200	-1.46820400
C	0.48066200	-0.19052200	-0.45685700
C	-2.24076500	0.67710300	-0.54342000
C	-1.91855500	-0.59784600	-0.05633600
C	-0.54033000	-1.01883800	-0.01542400
H	-3.27022200	1.01015200	-0.58003100
C	1.88609900	-0.66021300	-0.38757200
C	2.82218000	-0.06411200	0.47396700
C	2.31210400	-1.74381400	-1.15964300
C	4.14721800	-0.52213900	0.57042400
C	3.64043400	-2.22079200	-1.06797500

C	3.21076600	1.69041100	2.11157400
C	5.02076900	0.16237800	1.48119100
C	4.54436300	-1.62071500	-0.21867600
C	4.58118600	1.21186600	2.21376000
H	6.04848300	-0.17963600	1.57176100
H	5.56606600	-1.98526100	-0.15158600
H	5.21637300	1.74854300	2.90686600
O	-0.29103200	-2.24060600	0.48709100
H	-1.16629300	-2.60163800	0.72853200
O	1.45012800	-2.33530600	-2.01421500
H	1.91230800	-3.07849100	-2.43262500
O	3.90953600	-3.28964400	-1.88932300
H	4.81578900	-3.59307900	-1.75612500
O	2.38754500	0.99060900	1.21912100
O	-1.57435300	2.73197600	-1.43722100
O	2.72340800	2.61790400	2.71088600
O	-1.08050800	4.72544600	-2.30909200
O	-2.78364500	-1.47712600	0.38524900
H	-3.79759000	-0.98081800	0.65751300
O	-4.82504000	-0.39608400	1.01986200
O	-5.81452500	-1.15005600	0.41454800
C	-7.06406200	-0.86103700	1.06153700
C	-8.13277800	-1.67026500	0.35110200
H	-7.24442600	0.21771900	0.99194600
H	-6.97273300	-1.12965700	2.12030900
H	-8.19392300	-1.39352600	-0.70465800
H	-9.10471300	-1.47974500	0.81492200
H	-7.92181900	-2.74078900	0.41922900

TS2-opt

C	-1.39299600	0.01553800	-0.85036200
C	-0.75303800	1.23779100	-0.61581300
C	0.57307500	1.31993800	-0.20407100
C	1.28767600	0.08570700	-0.03201000
C	0.64811000	-1.18220900	-0.24735700
C	-0.68074700	-1.17338000	-0.65440900
H	-1.32967700	2.14266900	-0.76040300
H	-1.19853200	-2.10749300	-0.83312700
O	2.54054200	0.10074500	0.40891300
H	3.36016300	0.27832100	-0.31149700
C	1.23146400	2.68599200	0.05800200
C	2.31155100	2.96329800	-1.01264500
H	2.74395200	3.95626000	-0.84701600
H	3.12436500	2.23875800	-0.99238900

H	1.86838200	2.95262200	-2.01393400
C	1.85557200	2.73572300	1.47235100
H	2.65341300	2.00493000	1.58692400
H	2.26466600	3.73528200	1.65367700
H	1.09416100	2.54017100	2.23501000
C	0.20483400	3.83291300	-0.02159200
H	-0.23074100	3.93184500	-1.02067700
H	-0.60786800	3.70643800	0.70096300
H	0.70886600	4.77612300	0.20744600
C	1.40615400	-2.50542600	-0.04696800
C	1.96428700	-2.59784700	1.39263000
H	2.47958200	-3.55555800	1.52526100
H	2.66035000	-1.78788700	1.60333500
H	1.14988200	-2.55103900	2.12337500
C	2.55311600	-2.61361200	-1.07712000
H	3.27754500	-1.80623700	-0.98318100
H	3.08164500	-3.56404600	-0.94169600
H	2.15348100	-2.59519200	-2.09632400
C	0.48872200	-3.72540600	-0.25521500
H	-0.35263700	-3.73033300	0.44508500
H	0.09252800	-3.77528800	-1.27416700
H	1.06639000	-4.63846600	-0.08419800
C	-2.84714100	-0.02121000	-1.24305200
H	-3.10345900	0.85442900	-1.84690800
H	-3.05523100	-0.89822100	-1.86309700
C	-3.75860000	-0.05779100	-0.00831200
H	-3.53428300	-0.92924300	0.61775300
H	-3.58710100	0.81533000	0.63167300
C	-5.22696800	-0.10041300	-0.37510300
O	-5.99882100	-0.11601100	0.73182400
C	-7.42627600	-0.15858100	0.50050600
H	-7.66175200	-1.05184600	-0.08601200
H	-7.71228300	0.71149600	-0.09823200
C	-8.10360200	-0.16861000	1.85553300
H	-7.84939000	0.72965400	2.42492400
H	-9.18977900	-0.20063500	1.72801800
H	-7.79857700	-1.04282600	2.43727900
O	-5.66795000	-0.11939100	-1.50450000
C	7.05140900	-0.41684700	1.38212500
H	7.81379000	0.25553600	0.97984700
H	7.53808100	-1.34628000	1.69143200
H	6.60626700	0.05009600	2.26476100
C	5.99091300	-0.71733700	0.33978200
H	6.41094300	-1.16962400	-0.56547600

H	5.20797400	-1.37900600	0.72831700
O	5.38421500	0.53766700	-0.02035800
O	4.44073800	0.32447400	-1.00439800

TS3-opt

C	1.07470600	1.21481800	1.44559600
C	-0.16861400	1.12664800	0.84732300
C	-0.37968600	0.20919000	-0.21174500
C	0.68707800	-0.62745500	-0.65231700
C	1.92614000	-0.53423800	-0.00190500
C	2.11997000	0.38149700	1.04561900
H	1.23552800	1.91631400	2.25766100
H	-0.98511700	1.75467800	1.17533400
H	3.08026000	0.42919300	1.53812000
C	0.48372300	-1.59147100	-1.79000800
H	0.30287800	-2.61102400	-1.42722100
H	-0.38507100	-1.30759000	-2.38309200
H	1.35855600	-1.61189300	-2.44721300
C	-2.65589800	0.91993100	-0.73990800
O	-3.82513900	0.57276300	-0.71612800
O	-2.26528500	2.21626200	-0.78478200
C	-3.34099100	3.18008400	-0.82035500
H	-3.96477300	2.98053100	-1.69678000
H	-3.96785300	3.04632300	0.06635500
C	-2.70579400	4.55460300	-0.87168600
H	-2.07650500	4.65921800	-1.75957200
H	-3.48452900	5.32228800	-0.90639900
H	-2.08604300	4.73168800	0.01181700
N	2.94567400	-1.42558300	-0.39605300
H	2.65918600	-2.29671500	-0.81646900
C	4.31464200	-1.27794000	-0.43689700
O	5.05379700	-2.15139200	-0.84948400
O	4.72521200	-0.07522100	0.01671600
C	6.15434800	0.13880600	-0.03356700
H	6.65058000	-0.65184200	0.53597400
H	6.48546900	0.05635900	-1.07272500
C	6.41852100	1.51468600	0.54221300
H	6.08763300	1.57359200	1.58303900
H	7.49068200	1.72955900	0.51011800
H	5.89427800	2.28398600	-0.03123200
H	-2.04130500	-1.19303200	-0.70584700
O	-2.30863000	-2.28728900	-0.46595200
O	-3.31825700	-2.25961000	0.48892200
C	-4.59247200	-2.38522800	-0.16791800

C	-5.65103100	-2.10231400	0.88112500
H	-4.67345200	-3.39982800	-0.57842800
H	-4.62943300	-1.65644800	-0.98029100
H	-5.55770900	-2.78369400	1.73178200
H	-6.64639800	-2.23011200	0.44539300

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