Eco-efficient fractionation of bamboo using a pyruvic acid-based deep eutectic solvent: a waste-minimized strategy for comprehensive valorization

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1. Experimental section

1.1. Characterizations

Thermogravimetric analyzer (TG209F3, Germany) was used to analyze the thermal properties of cellulose-rich residue. At nitrogen atmosphere, each sample was heated from 40 to 800 ℃ at a rate of 15 ℃·min^{-1}. Comprehensive pyrolytic index (CPI) was used to evaluate the pyrolytic severity and calculated using the following equation:[1, 2]

$$CPI = \frac{-DTG_{max}}{T_{max}(T_e - T_i)}$$

T_i represents starting temperature of devolatilization; T_{max} represents the peak temperature on the DTG curve; T_e represents end temperature of devolatilization; DTG_{max} represents the maximum degradation rate on the DTG curve.

The kinetic parameters of material pyrolysis within the temperature range of 150-380 °C were determined according to previous research.[3]

$$\frac{d_\alpha}{d_T} = \frac{A}{\beta}\exp(-\frac{E}{RT})F(\alpha)$$

where α represents the conversion rate; E represents the activation energy; A represents the pre-exponential; β represents the heating rate; T represents response temperature; $F(\alpha)$ represents kinetics equation, and R represents the gas constant.

Tensile tests on the bio-plastics were performed using an Instron 3300 universal testing machine. The films were precisely cut into rectangular samples measuring approximately 10 × 50 mm². These samples were clamped at both ends and stretched along the longitudinal direction at a constant strain rate of 5 mm/min until fracture occurred. Fourier transform infrared spectroscopy (ATR-FTIR) was conducted using a NICOLET IS50 spectrometer (Thermo Fisher Scientific, USA) with a scanning range of 4000-650 cm^{-1} and a resolution of 4 cm^{-1}. The UV-visible (UV-vis) spectral analysis of the bio-plastics was conducted with a spectrophotometer (UV-2600, Japan), scanning wavelengths from 200 to 800 nm. The UV-blocking capability of composite films was calculated via the following equation:

$$\text{UV blocking (\%)} = \left(1 - \frac{\int_a^b T(\lambda)d\lambda}{\int_a^b d\lambda}\right) \times 100\%$$

In the equation, T(λ) represents the average spectral transmittance of the bio-plastics, where dλ denotes the bandwidth and λ is the wavelength. The integral limits for calculating overall UV blocking are set as a=200 nm, b=400 nm. When calculating for UVA blocking, the range is 320-400 nm. For UVB blocking, the range is 290-320 nm.

Table S1. Pyrolysis parameters and kinetics of bamboo feedstock and pretreated residues.

Samples	Pyrolysis parameters						Kinetic parameters		
	T_i (°C)	T_{max} (°C)	T_e (°C)	Weight loss (%)	DTG_{max} (%/min)	CPI [× 10^{-5} (%/min °C^2)]	E^a (kJ/mol)	Log A (s^{-1})	R^2
Bamboo	151.86	352.14	380.42	82.44	-9.49	11.79	60.75	2.69	0.999
PyA-R_{80}	156.40	344.75	371.56	88.92	-20.53	27.68	94.3	5.15	0.999
PyA-R_{100}	157.66	339.48	365.71	91.52	-28.85	40.85	169.55	12.26	0.999
PyA-R_{120}	160.23	336.94	365.88	91.16	-31.02	44.77	211.89	16.07	0.998
PyA-R_{140}	163.32	337.59	366.99	92.01	-32.55	47.34	240.13	18.54	0.999
AA-R_{140}	158.29	350.27	375.88	90.95	-25.68	33.69	149.28	10.23	0.998
PA-R_{140}	164.19	345.80	373.22	89.15	-23.51	32.53	118.75	7.62	0.998

T_i: Initial temperature of devolatilization;

T_{max}: The peak temperature on the DTG curve;

T_e: End temperature of devolatilization;

DTG_{max}: The maximum weight loss rate;

CPI: Comprehensive pyrolytic index;

[a] Temperature range between 150 °C and 380 °C.

Table S2. Semi-quantitative evaluation of PMI and E-factor.

Parameter	Scenario A	Scenario B
Total Input Mass:	1120.9 g	1120.9 g
Recovered ethanol	75.0 g	75.0 g
Desired Products	1.35 g	42.0 g
Total Waste*	1044.55 g	1003.9 g
PMI	830.3	26.69
E-factor	773.7	23.90

Scenario A (Traditional strategy): The xylose-enriched DES filtrate is discarded as waste.

Scenario B (Our proposed strategy): The xylose-enriched DES filtrate is upcycled as functional additives for plastic films.

*: Total Waste = Total Input-Recovered ethanol-Desired Products.

Table S3. Chemical compositions and their concentrations in the waste-DES filtrate.

Chemical compositions	Concentrations ($mg\cdot L^{-1}$)
Glucose	126.5
Xylose	212.9
Arabinose	13.5
HMF	21.5
Soluble lignin	65.2
Pyruvic acid*	31.6×10^3
Choline chloride*	8.36×10^3

*: Estimated based on mass balance.

Table S4. The comparative analysis of the thermochemical properties

Method	DTG_{max} (%/min)	CPI [× 10^{-5} (%/min °C^2)]	E (kJ/mol)	Reference
Microwave assisted organosolv pretreatment	-39.38	-	291.6	4
Benzenesulfonic acid pretreatment	-8.32	-	103.9	5
Acid washing pretreatment	-20.9	41.8	140.9	2
Torrefaction pretreatment	-22.0~-26.6	19.9~48.3	-	1
Electro-assisted seawater pretreatment	-8.3~-10.7	6.9~10.2	71.5~119.8	6
PyA-DES pretreatment	-20.5~-32.6	27.7~47.3	94.3~240.1	This work

Table S5. The summary of lignocellulose fractionation with different DES systems

Feedstock	DES	Pretreatment condition	Delignification efficiency (%)	Cost*	Ref.
Poplar	$ZnCl_2$/Lactic acid	120 °C, 3 h	96.3	~$1.1–1.2/kg	7
Reed straw	BTEAC/Formic acid	130 °C, 3 h	78.1	~$2.5–4.4/kg	8
Boehmeria nivea stalks	Betaine/Glyoxylic acid	130 °C, 2 h	81.9	~$2.1–3.0/kg	9
Moso bamboo	Betaine/Levulinic acid	80 °C, 2 h	11.7	~$3.3–4.1/kg	10
Eucalyptus	ChCl/Vanillin/$FeCl_3$	135 °C, 2 h	97.1	~$10.4/kg	11
Corn straw	ChCl/3-(4-hydroxyphenyl)propionic acid	160°C, 4h	58	~$22–55/kg	12
Switchgrass	ChCl/p-Coumaric acid	160°C, 3h	60.8	~$8.4–16.6/kg	13
Poplar	ChCl/p-Hydroxybenzaldehyde	160°C, 3h	30.7	~$4.0–6.7/kg	14
Bamboo	ChCl/Pyruvic acid	100°C, 1h	98.12	~$6.5–8.1/kg	This work

*: The estimated DES costs were calculated from the weighted prices of the corresponding HBA and HBD components based on their molar ratios.

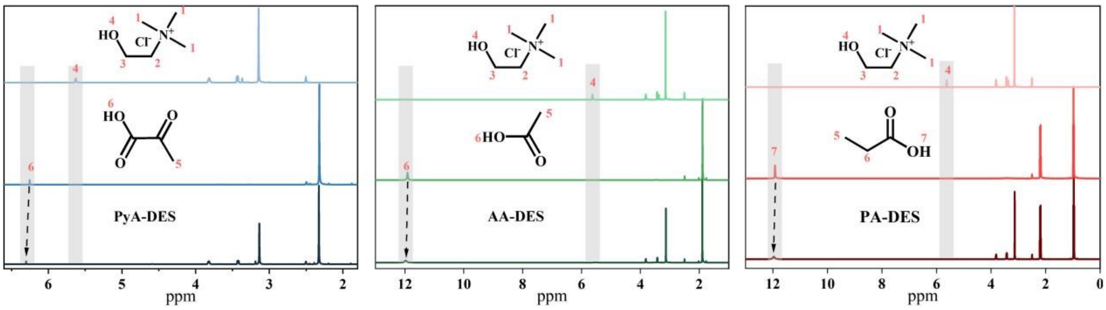

Fig. S1. ^{1}H NMR spectra of of various DES systems (PyA-DES, AA-DES, and PA-DES).

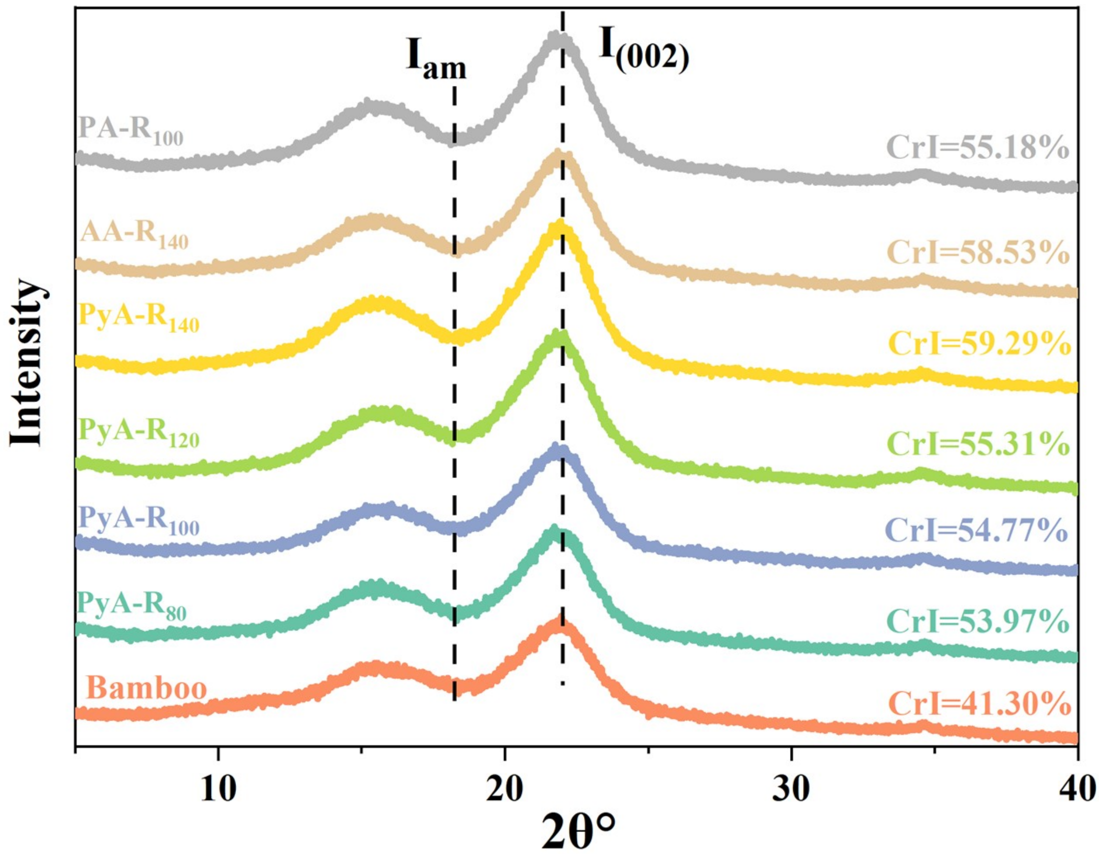

Fig. S2. XRD spectra of bamboo feedstock and pretreated residues.

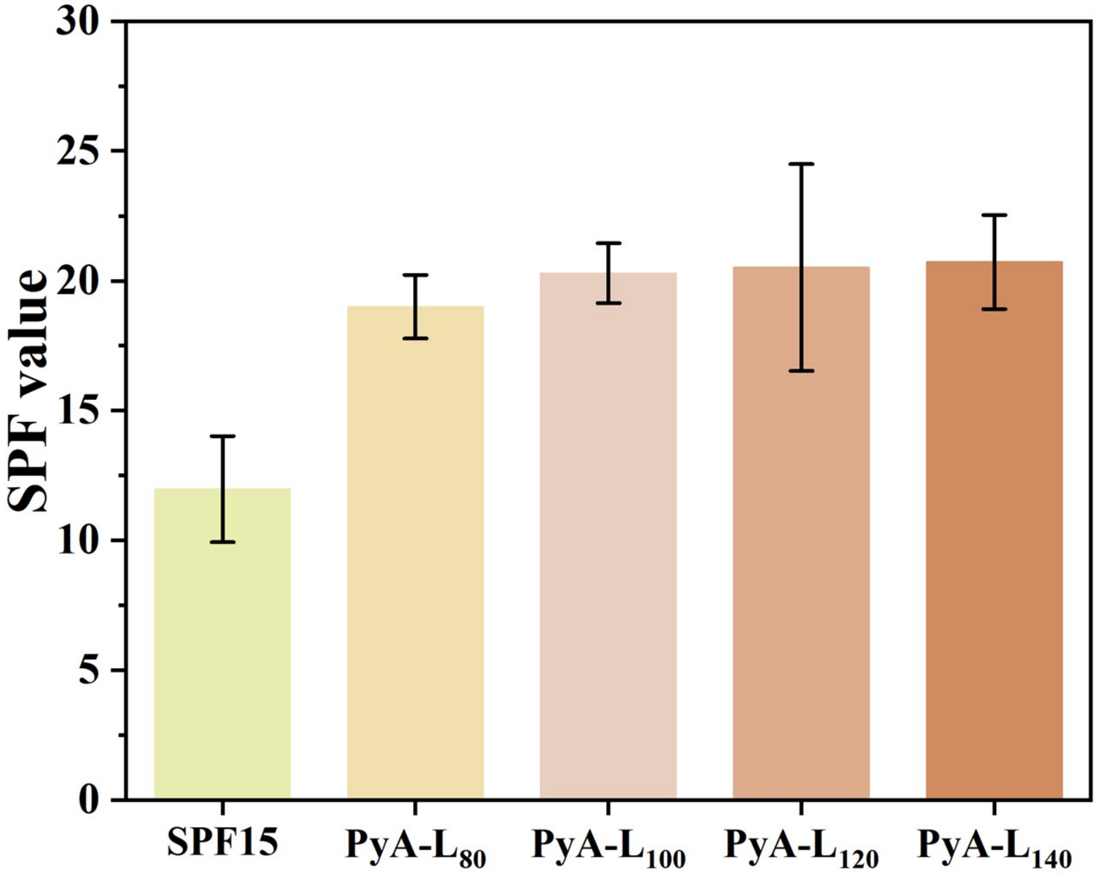

Fig. S3. The SPF values of lignin-based sunscreens from various lignin fractions.

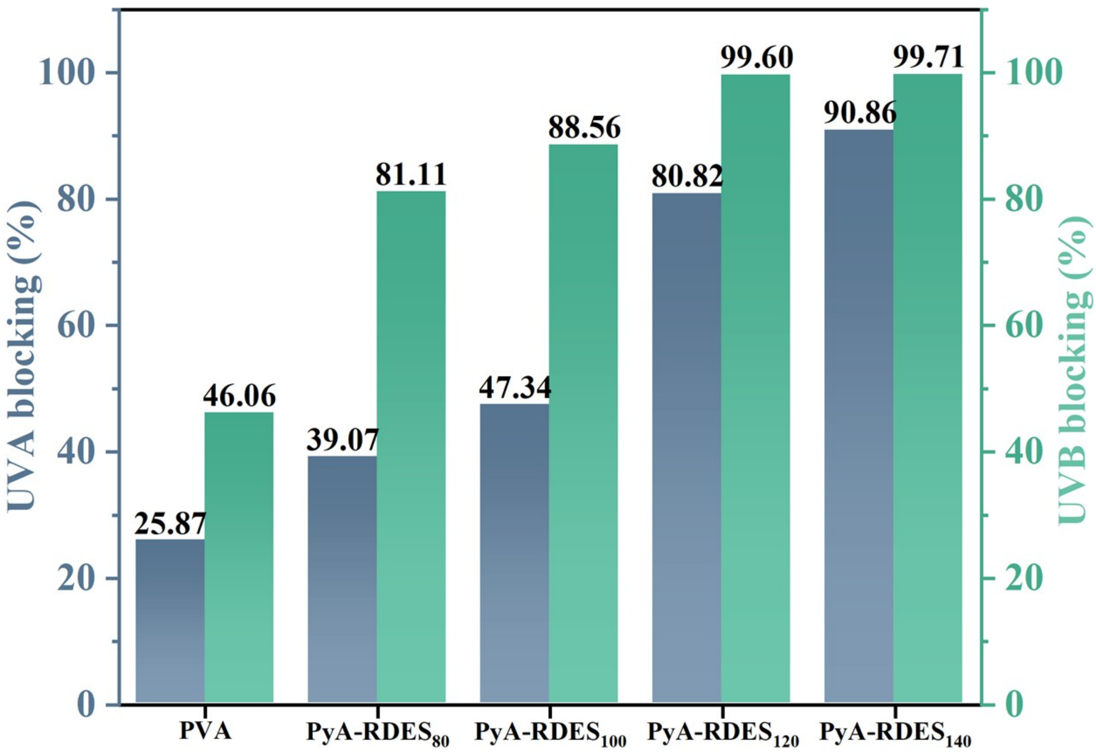

Fig. S4. UV blocking of bio-plastic films.

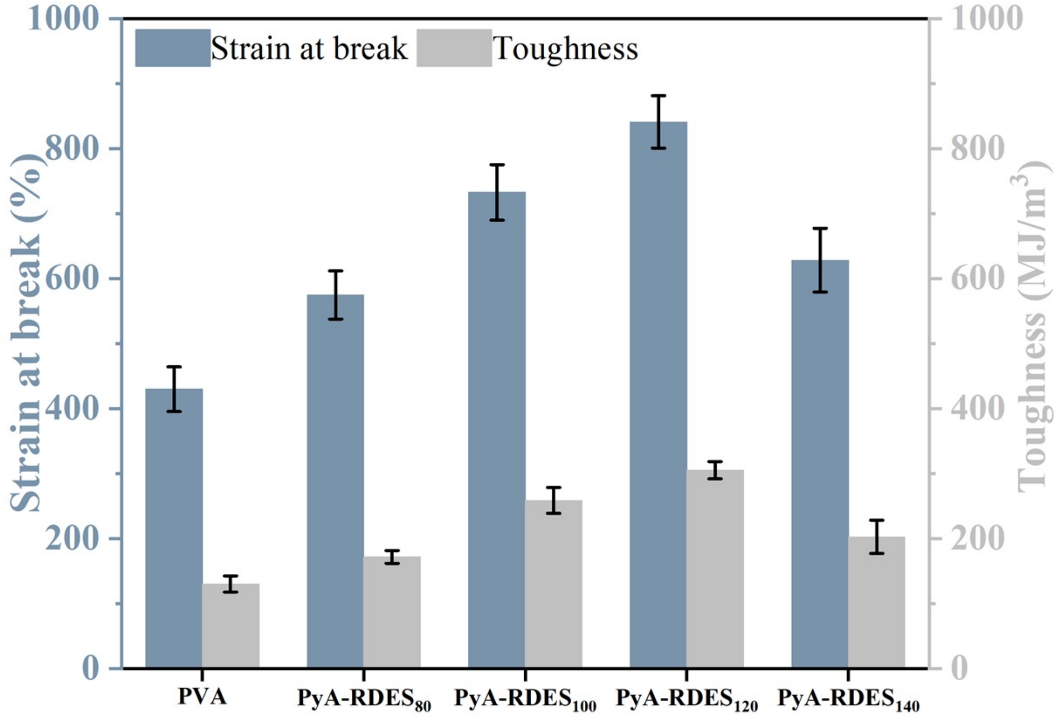

Fig. S5. Elongation at break and toughness of bio-plastic films.

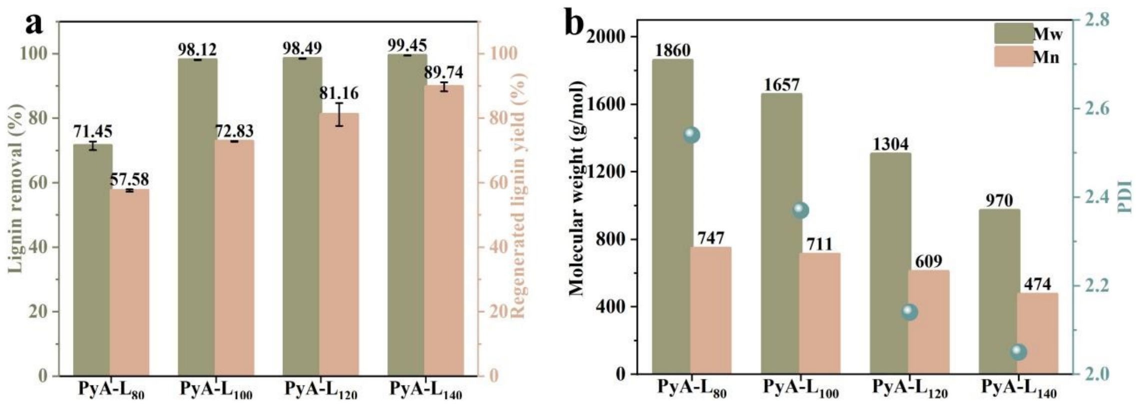

Fig. S6. (a) The lignin removal and the recovery yield of regenerated lignin; (b) molecular weight and polydispersity index of regenerated lignin.

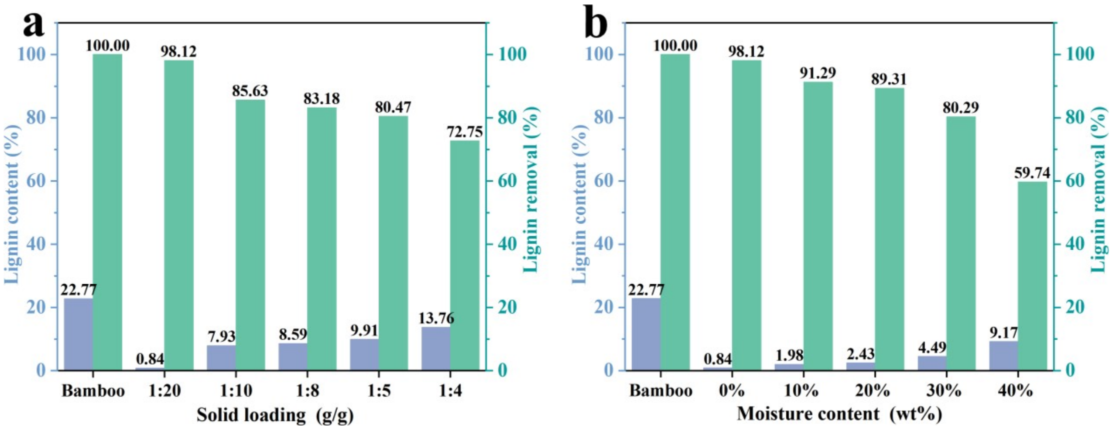

Fig. S7. Effect of solid loading (a) and moisture content (b) on the lignin content and delignification efficiency during PyA-DES pretreatment.

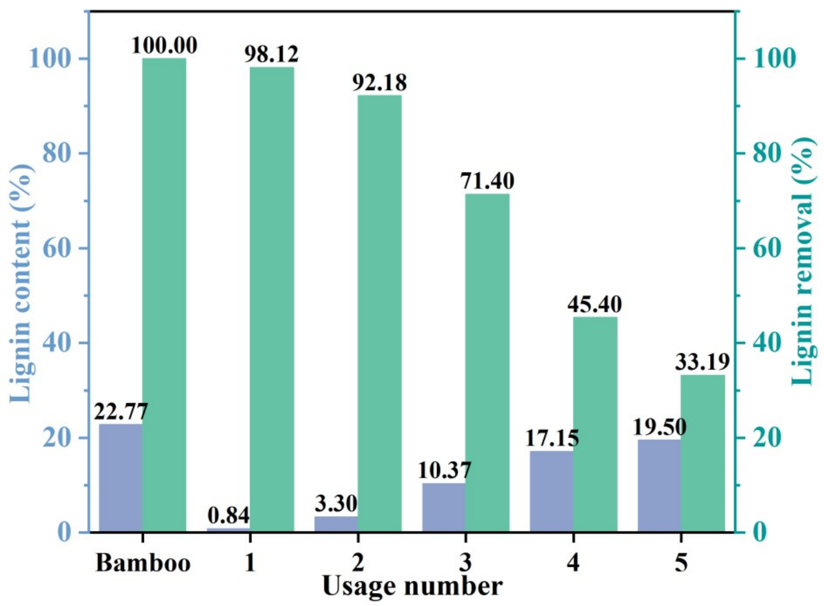

Fig. S8. Effect of usage number on the lignin content and lignin removal of bamboo by PyA-DES pretreatment.

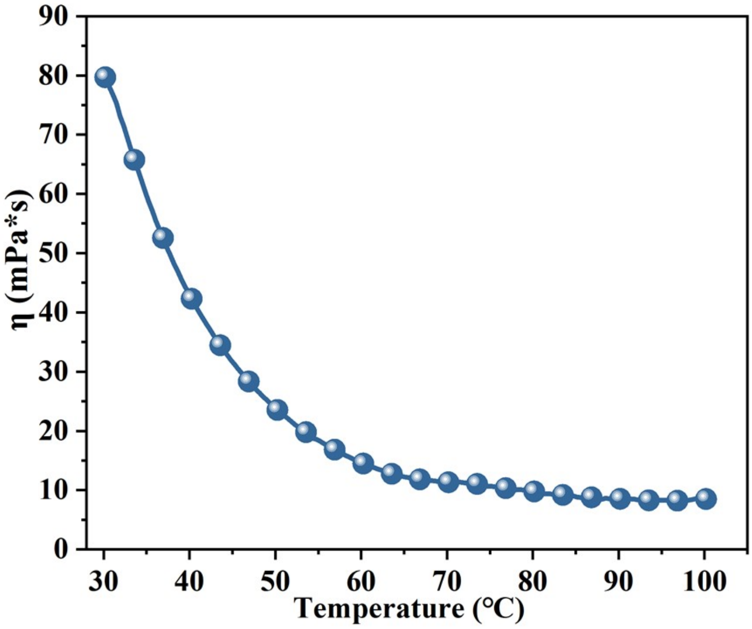

Fig. S9. Effect of temperature on the viscosity of PyA-DES.

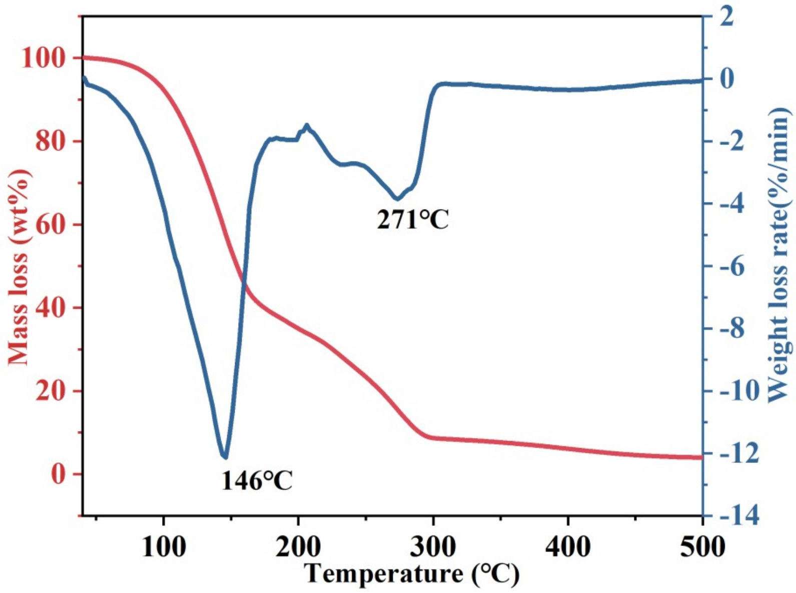

Fig. S10. The TGA analysis of PyA-DES.

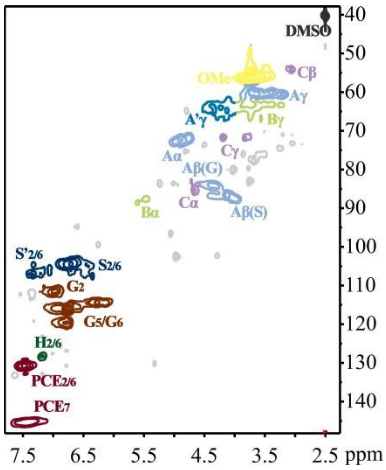

Fig. S11. The 2D HSQC NMR spectra of MWL from untreated bamboo.

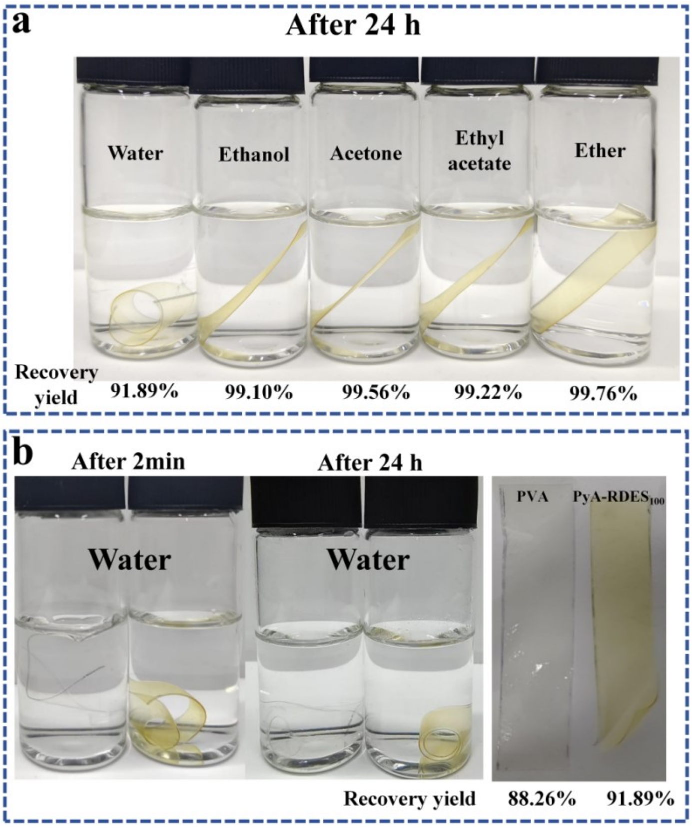

Fig. S12. Optical photos of bio-plastic film soaked in different solvents for 24 h.

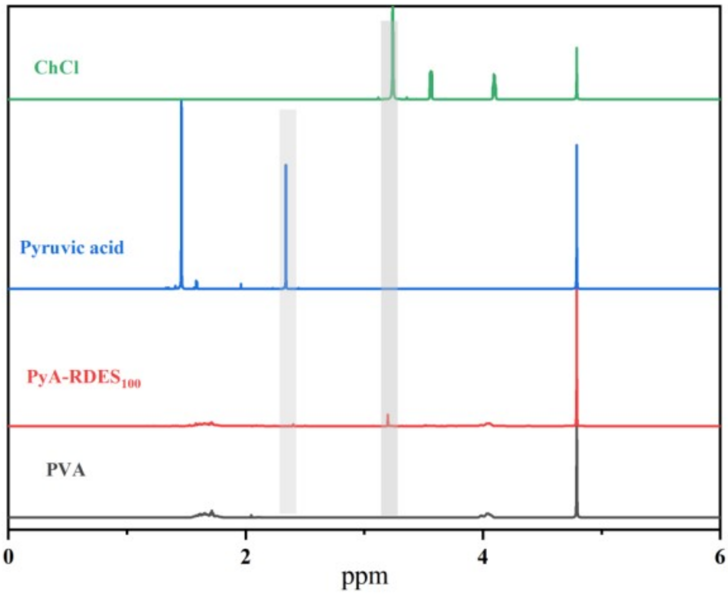

Fig. S13. [1]H NMR spectrum.

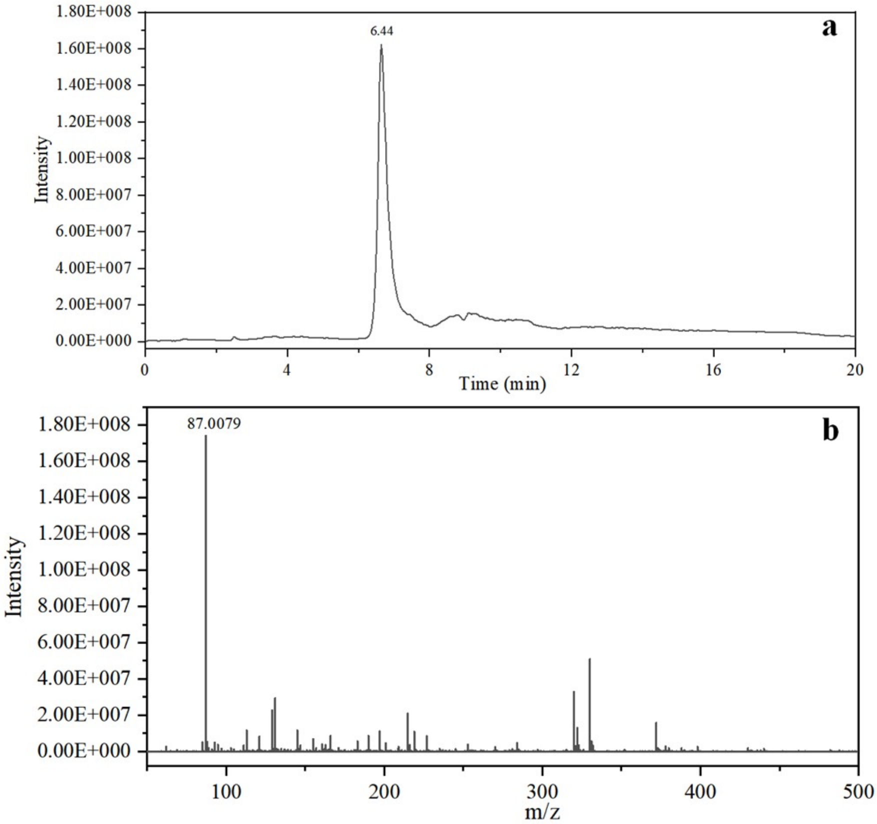

Fig. S14.(a) Negative ion total ion current diagram; (b) primary mass spectrum diagram.

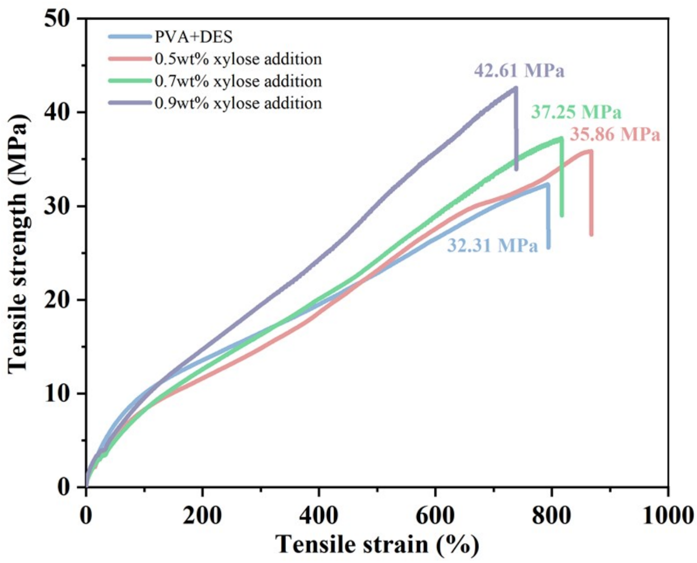

Fig. S15. Tensile stress-strain curves of PVA films.

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