Electronic Supplementary Material (ESI) for Green Chemistry.

Affinity of K^+ to Organic Matter Promotes Reactions: Degradation of Super Stable Phenolic Epoxy Vinyl Ester Resin to Value-added Chemicals

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1. Characterization methods:

1.1 Changes of functional group in the degradation products: FT-IR spectra were collected on Vertex 80 V (VRUKER, Germany) spectrometer in the range of 4000-400 cm^{-1} wavenumber with 40 scans.

1.2 Chemical structure of the degradation products: ^{13}C NMR and ^{1}H NMR was carried out on a Bruker AVANCE III 400 MHz spectrometer operation at 100-MHz frequency, The deuterated solvent selected is DMSO-d_6.

1.3 The content of potassium acetate and ethyl acetate was characterized by quantitative NMR (1D ^{1}H NMR): In all the NMR analyses, pyrazine was applied as the internal standard substance. The content of potassium acetate and ethyl acetate was calculated by the following **formula (2):**

$$m(x) = P(std)\frac{MW(x)\ nH(std)m(std)\ A(x)}{MW(std)\ nH(x)\quad P(x)\ \ A(std)} \qquad \textbf{(2)}$$

where m(x) and m(std) were the weights of analyte and internal standard substance, respectively, MW(x) and MW(std) were the molecular weights of analyte and internal standard substance, respectively, nH(x) and nH(std) were the number of protons that generated the selected signals for integration of analyte and internal standard substance, respectively, P(x) and P(std) were the purity of analyte and internal standard substance, respectively, A(x) and A(std) were the selected peak areas of analyte and internal standard substance, respectively.

1.4 The conversion ratio of methyl acetate was characterized by quantitative NMR (1D ^{1}H NMR): M_0 was the total methyl acetate added (g). M_1 was the mass of residual methyl acetate after reaction (g). the conversion ratio was calculated by the **formula (3):**

$$\text{Conversion ratio}\ (\%) = \frac{M_0 - M_1}{M_0} \times\ 100\% \qquad \textbf{(3)}$$

1.5 Element content of K and Na inside resin was determined by Inductively Coupled Plasma Optical Emission Spectrometer (Aglient5110, America). Instrument parameters: Pump Rate: 100 r/min, Low WL Range: 10 s, High WL Range: 5 s, Nebulizer Flow: 28.0 psi, Auxiliary Gas: 0.5ipm, Sample Flush Time: 20 s, RF Power: 1150 w.

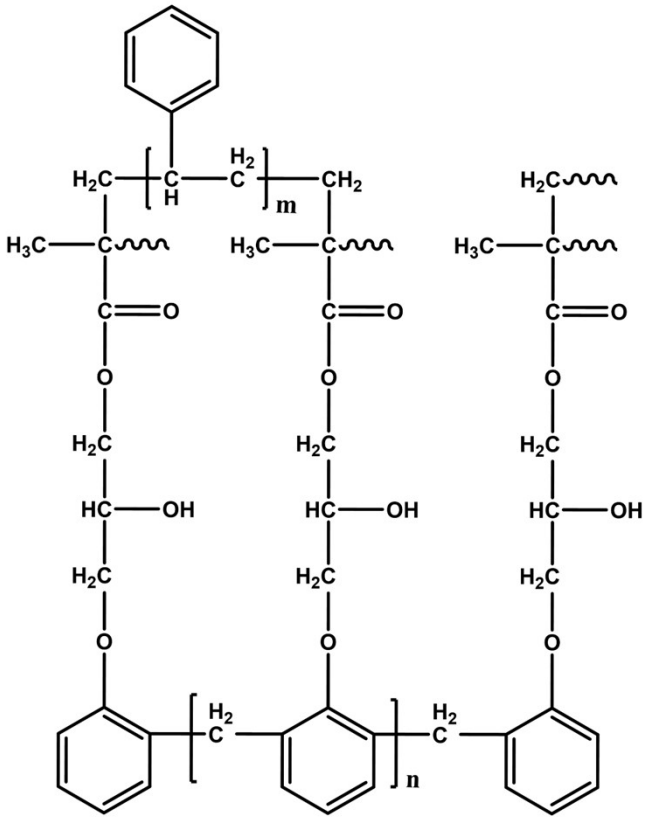

Figure S1 The molecular structure of phenolic epoxy vinyl ester resin (PEVER).

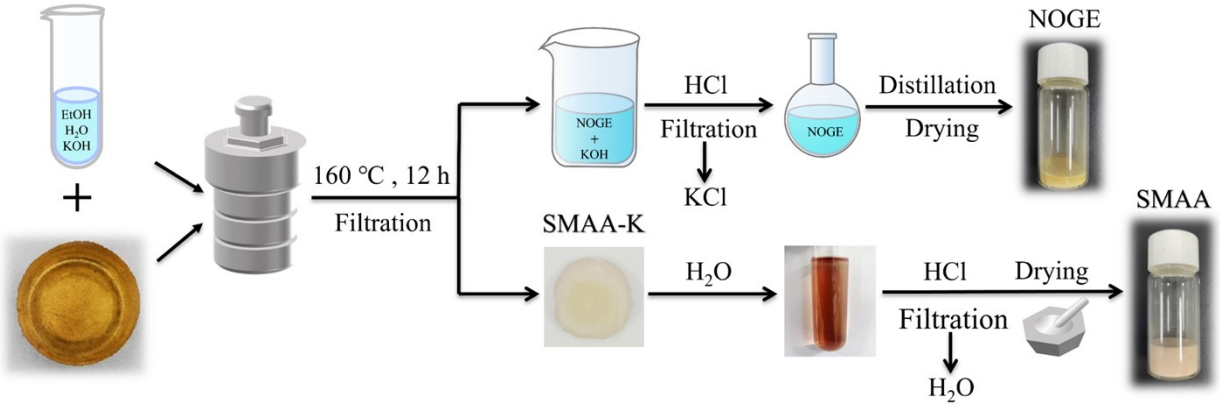

Figure S2 Experimental processes of PEVER degradation and product separation.

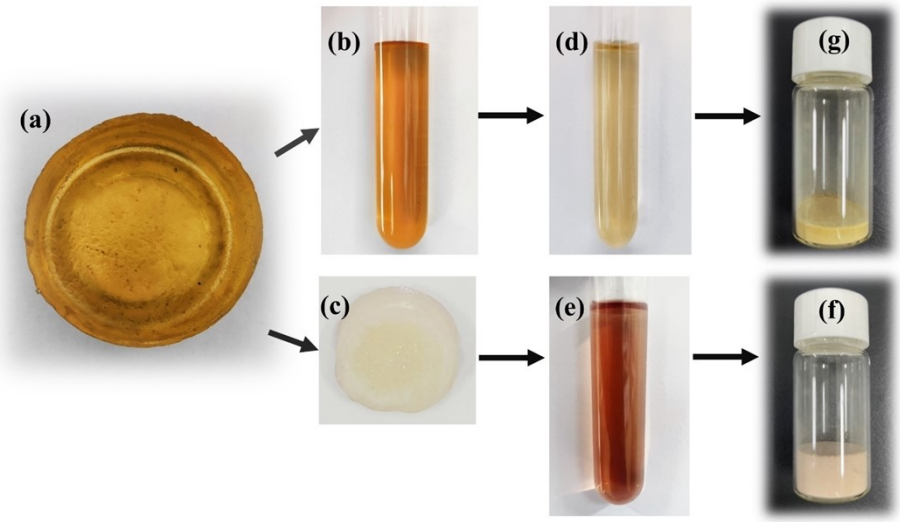

Figure S3 Photos of (a) original PEVER, (b) liquid 1, (c) solid 1, (d) liquid 2, (e) liquid 3, (f) SMAA, and (g) NOGE.

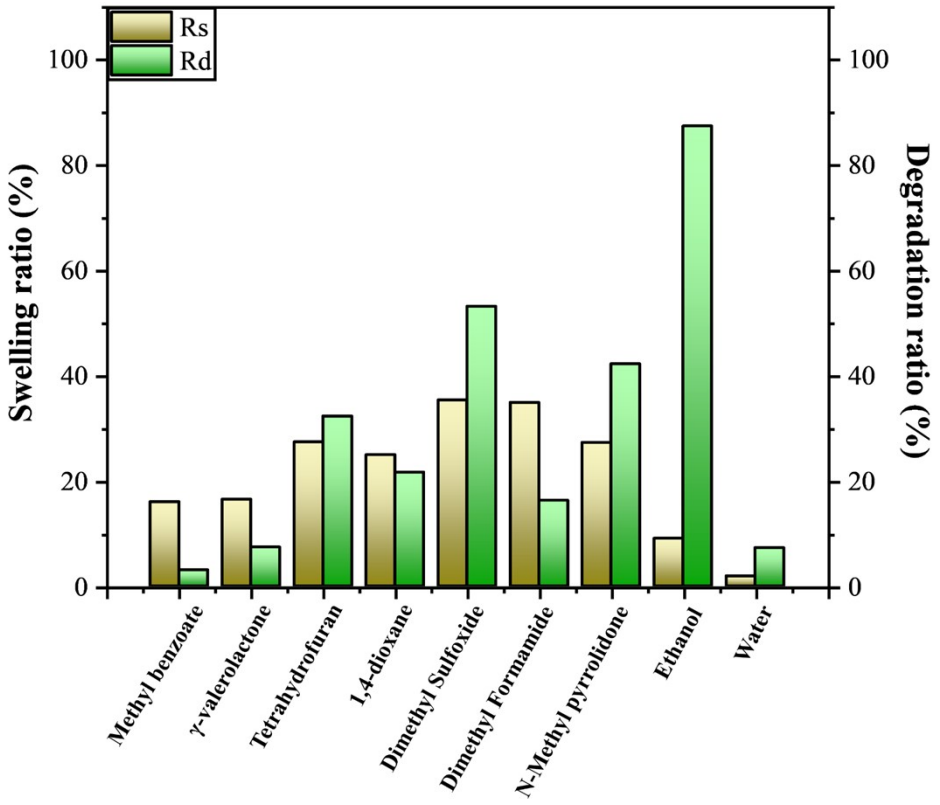

Figure S4 The swelling and degradation behaviors of PEVER in different solvents at 160 ℃ for 12 h. The swelling of PEVER was explored at the same conditions to the degradation of PEVER, except that no catalyst was present. Swelling experiment: No catalyst, 0.2 g of PEVER, 3 g of solvent system. Degradation experiment: 0.2 g of PEVER, 3 g of degradation system, mass ratio of solvent to water is 9:1, mass fraction of the catalyst: 10 wt%.

The swelling ratio (R_S) was calculated as follows. After each swelling experiment, the remaining solvent on the surface of resin was promptly adsorbed and removal by the filter paper, and its weight was recorded as W_S. The swelling ratio was calculated by the following **formula (4)**.

$$\text{Swelling ratio}\left(R_s\right) = \frac{W_s - W_0}{W_0} \times 100\% \qquad \textbf{(4)}$$

Where W_0 is the original weight of the resin before degradation.

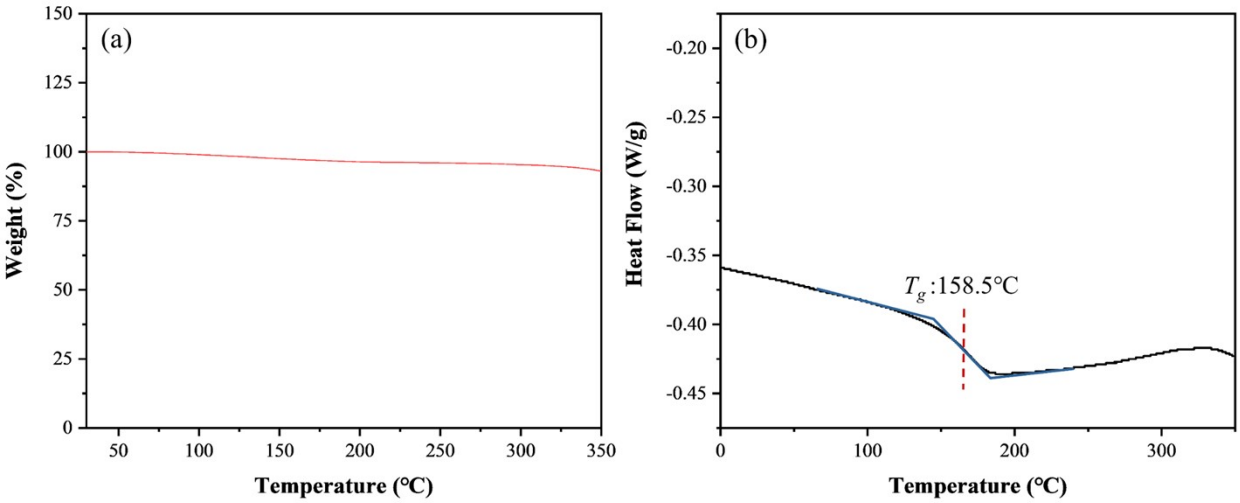

Figure S5 TG (a) and DSC (b) curves of PEVER.

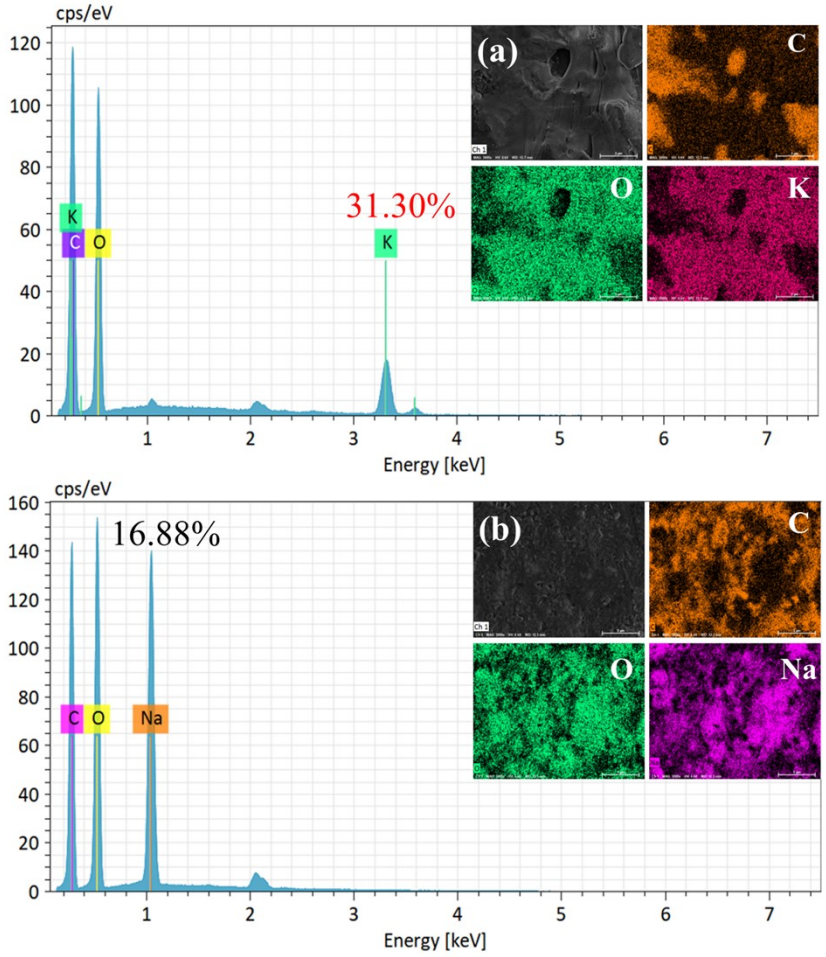

Figure S6 SEM-EDS analysis of PEVER after swelling at 140 ℃ for 4 h with: (a) KOH, x5000, and (b) NaOH, x5000.

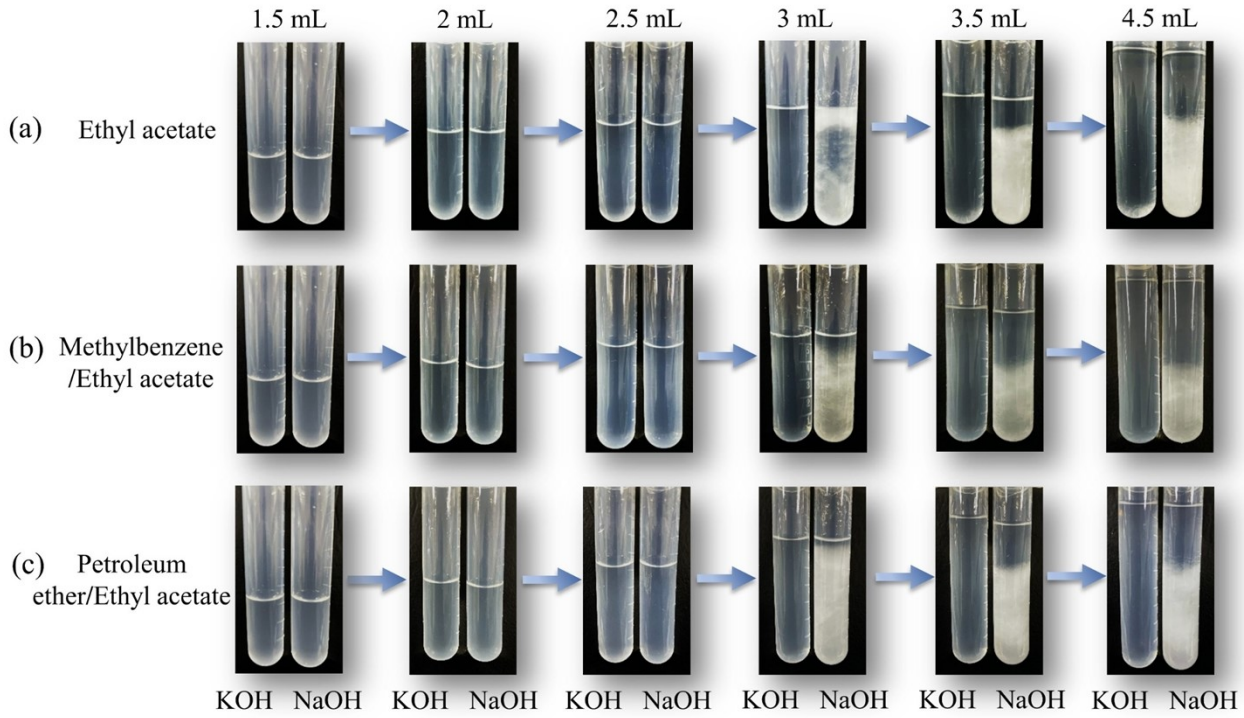

Figure S7 Precipitation behaviors of KOH and NaOH with addition of 1.5 mL to 4.5 mL of: (a) Ethyl acetate, (b) Methylbenzene + Ethyl acetate (the mass ratio of methylbenzene to ethyl acetate: 1:1), and (c) Petroleum ether + Ethyl acetate (the mass ratio of petroleum ether to ethyl acetate: 1:1). In each Experimental condition: 3 g of alkali/ethanol-H_2O degradation system with the mass ratio of ethanol to water of 9:1 and 0.0025 mol of KOH or NaOH.

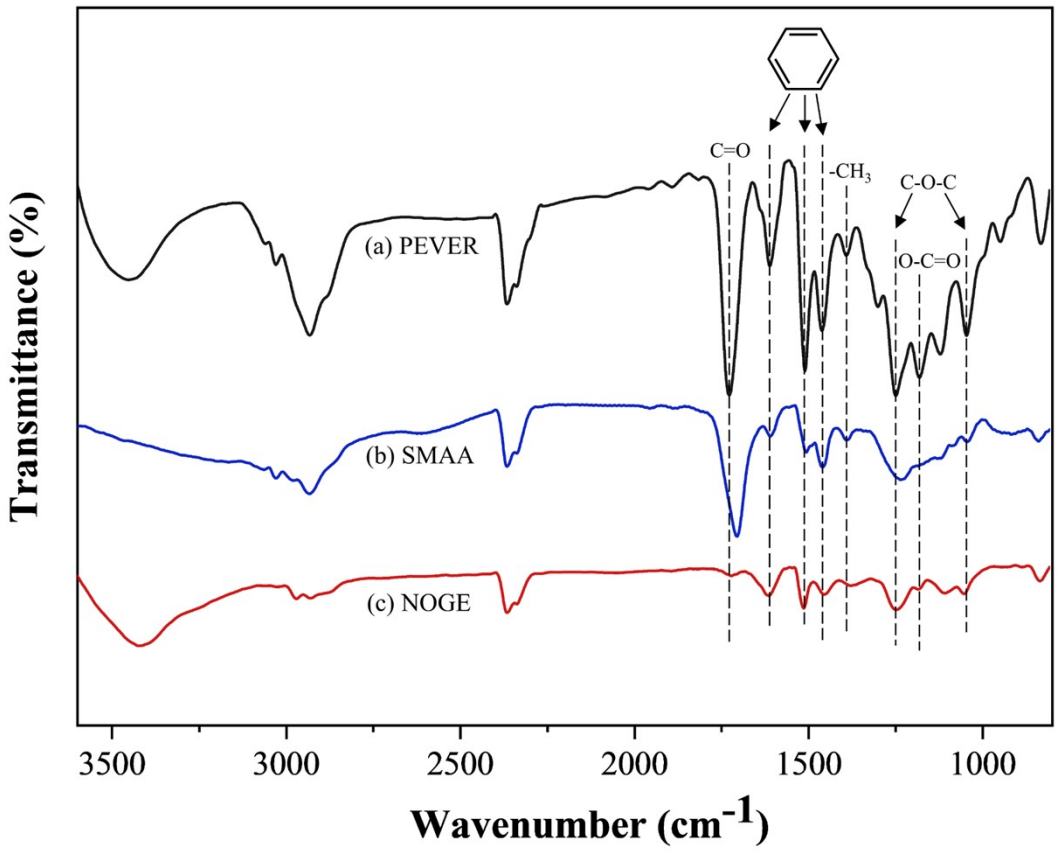

Figure S8 FT-IR spectra of PEVER and degradation products. (a) PEVER, (b) SMAA, (c) NOGE.

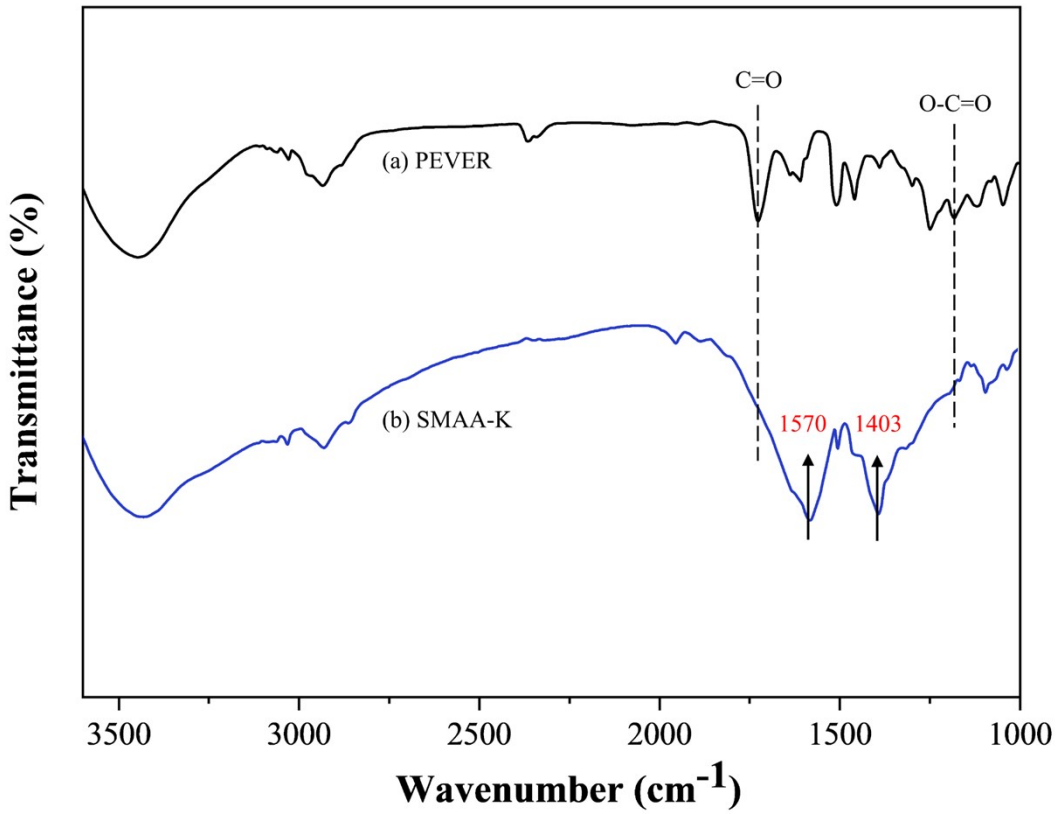

Figure S9 FT-IR spectra of PEVER and potassium salt of SMAA (SMAA-K). (a) PEVER, (b) SMAA-K.

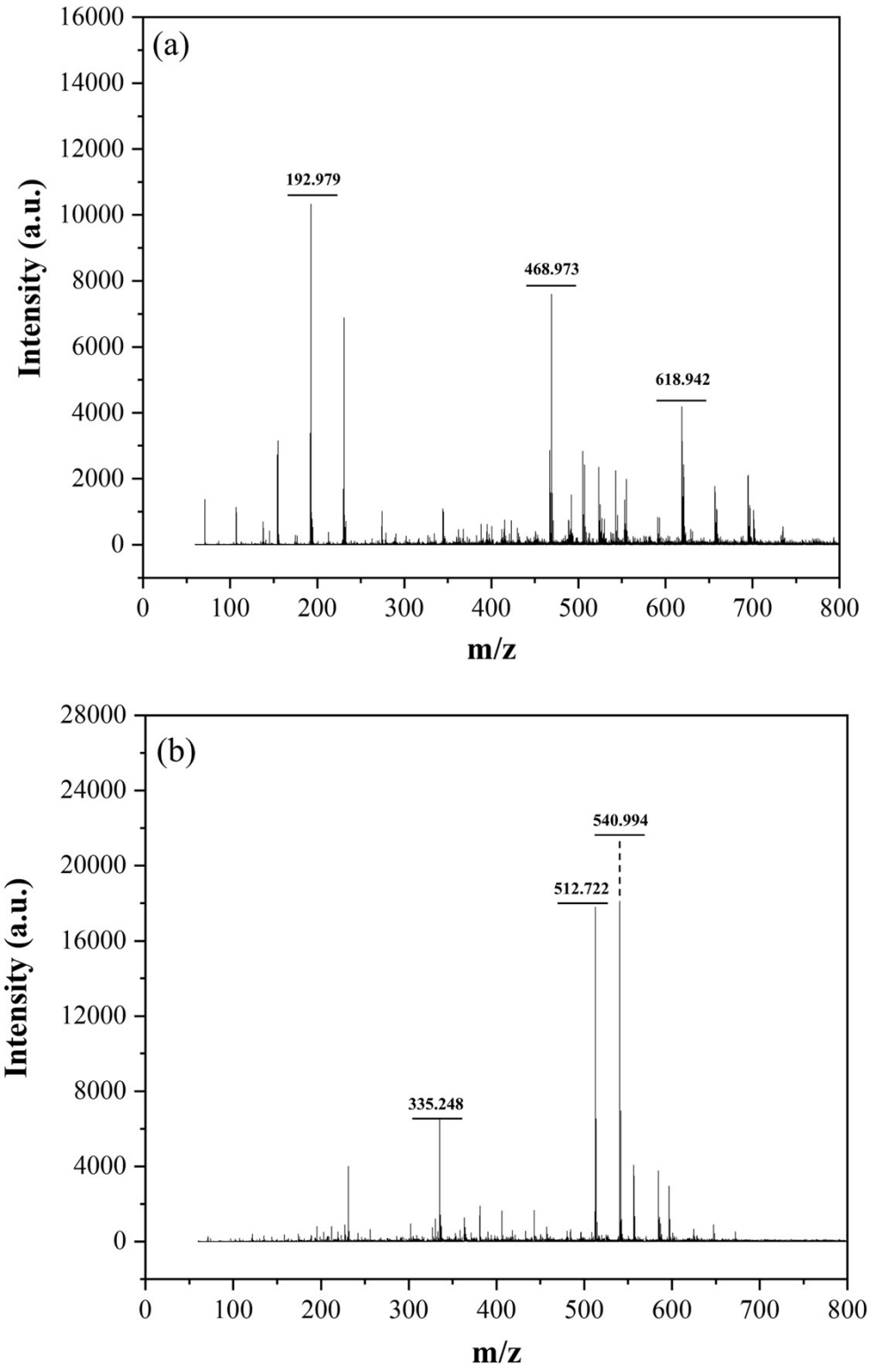

Figure S10 The time-of-flight mass spectrum of products. (a) SMAA, (b) NOGE.

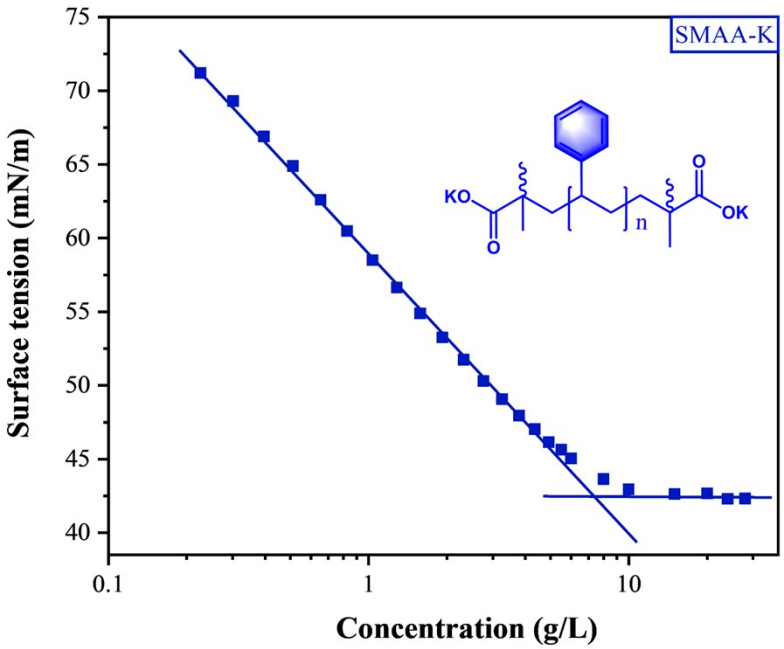

Figure S11 Correlation of the surface tension of aqueous solution (at 298.15 K) with the concentration of SMAA-K.

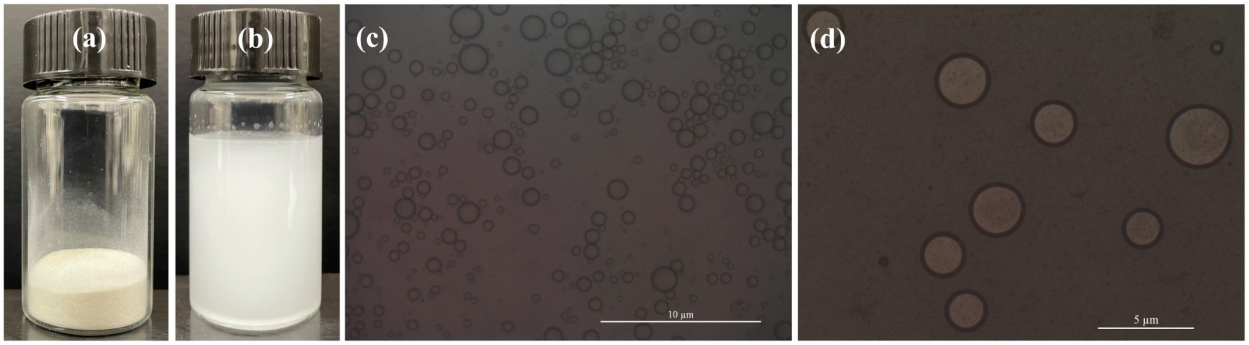

Figure S12 (a) SMAA-K, (b) emulsion, and photos of emulsion at a scale bar of 10 µm (c) and (d) 5 µm.

Figure S13 Photos of SMAA-K-containing emulsions with varied volume ratios of H_2O to petroleum ether.

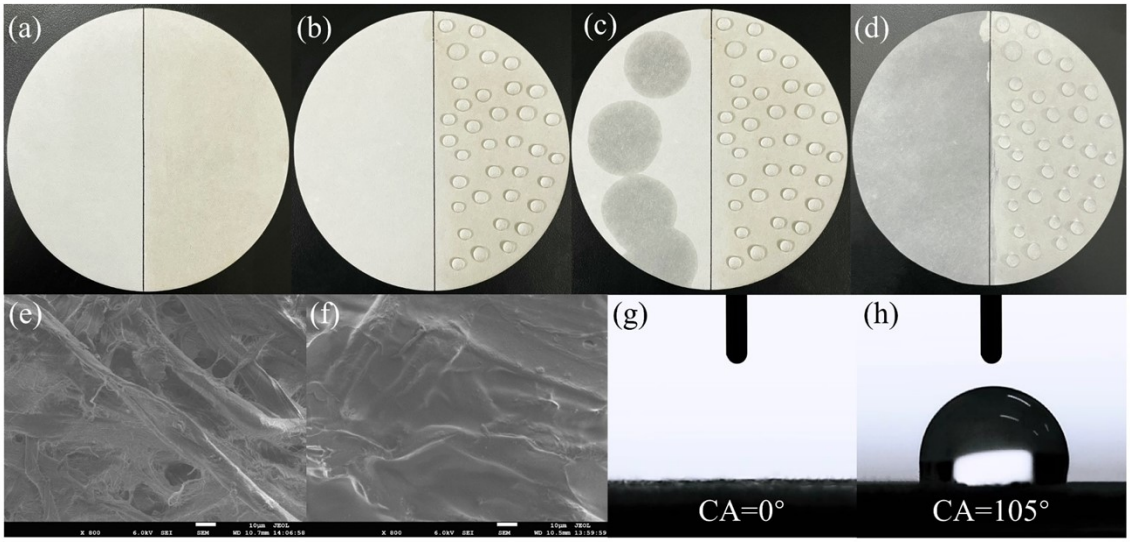

Figure S14 (a) Photos of filter paper and SMAA-modified filter paper, (b-d) Comparison of the pristine and SMAA-modified filter papers, SEM images of the pristine (e) and SMAA-modified filter papers (f), (g-h) Contact angles of water on the surface of the pristine (g) and SMAA-modified filter papers (h).

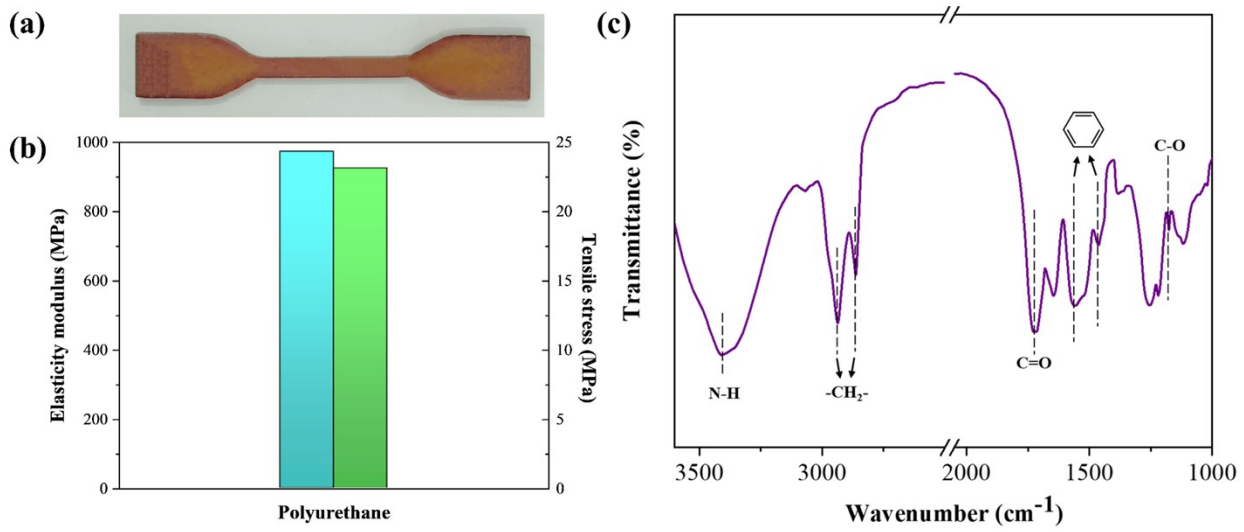

Figure S15 (a) Photos of new polyurethane material, (b) Mechanical properties of polyurethane, (c) FT-IR spectrum of polyurethane.

Table S1 The quality of different components after reaction [a]

Entry	Products	Mass/g	Mass ratio/%[b]
1	SMAA	0.1334	65.24
2	NOGE	0.0438	21.42

[a] Reaction conditions: 0.2 g of PEVER, 3 g of Degradation system, mass ratio of ethanol to water: 9:1, mass fraction of the KOH: 10 wt%, reaction temperature: 160 ℃, reaction time: 12 h. [b] The mass ratio is calculated in the case that n=2.

The mass ratio was calculated by following formula (5):

$$\text{Mass ratio}\ (\%) = \frac{W_1}{W_0 + \dfrac{W_{NOGE} \times (n+2)}{29.33 + 10\,(n-1)}} \times 100\% \qquad \textbf{(5)}$$

Where W_0 is the weight of PEVER, W_1 is the weight of SMAA or NOGE product after reaction, W_{NOGE} was the weight of the NOGE after reaction, and n represents the number of repeating units in the PEVER (see Figure S1). Generally, the value of n equals to 1 or 2.