Supporting Information

Polyurethane-urea Coatings Derived from UV-cured Polyurethane-urea Acrylate Transition Coatings for Enhanced Resistance to Chemical Warfare Agent Simulants

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Characterization of PUUA monomer TBEMA-Htri (Figure S1–S3)

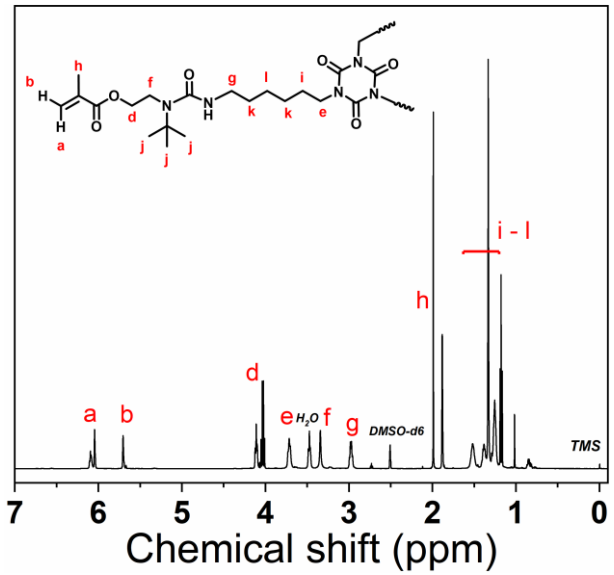


Figure S1. ^{1}H NMR of the PUUA monomer TBEMA-Htri

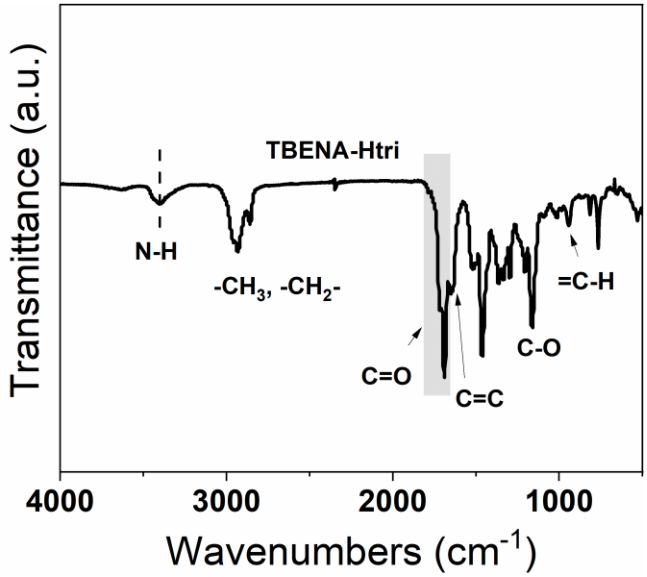


Figure S2. FTIR spectrum of the PUUA monomer TBEMA-Htri

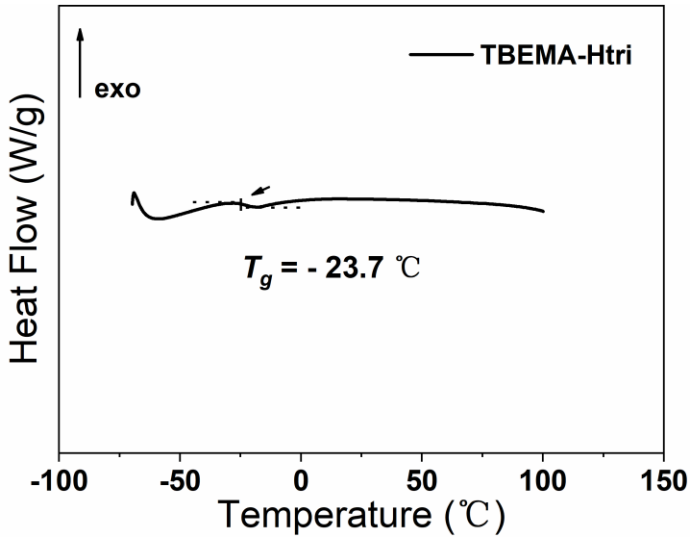


Figure S3. DSC curve of the PUUA monomer TBEMA-Htri

Table S1. Formulations of the dual cured PUUAs(PUUs)

Formula /g	TBEMA-Htri	IBOA	Diamine	TPO-L	184
PUUA-PEA	3.5	1.5	1.14	0.08	0.02
PUUA-DCHA	3.5	1.5	0.56	0.08	0.02
PUUA-IPDA	3.5	1.5	0.84	0.08	0.02
PUUA-HMDA	3.5	1.5	1.04	0.08	0.02

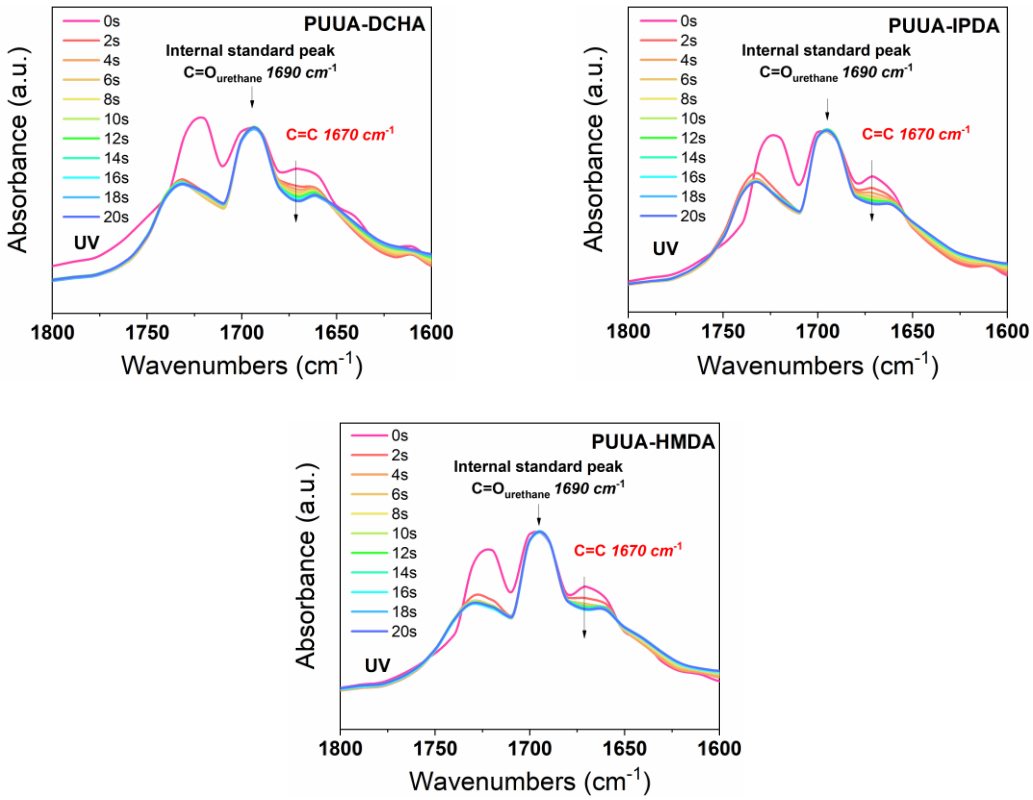


Figure S4. Dynamic FTIR spectra with UV light of PUUA-DCHA, PUUA-IPDA and PUUA-HMDA.

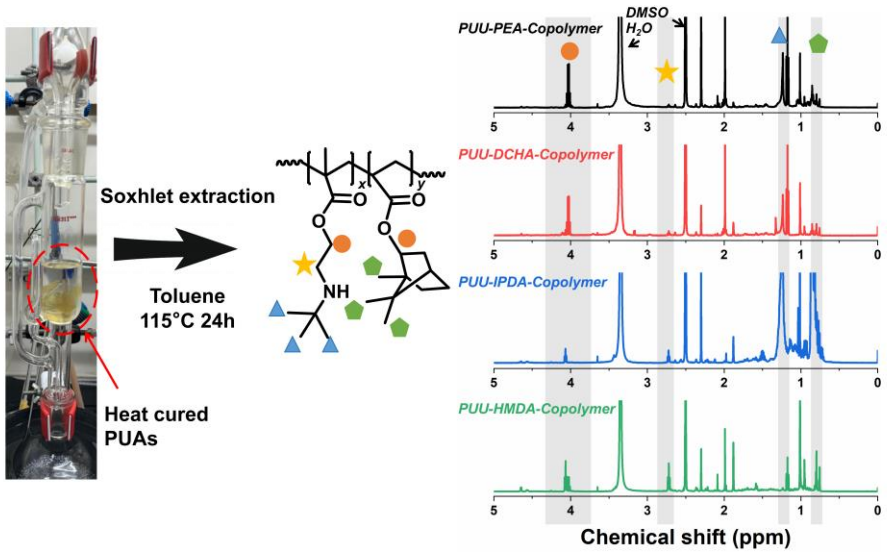


Figure S5. ^{1}H NMR spectra of the copolymer obtained by Soxhlet extraction

Figure S6. Photographs of the PUUA and PUU coatings

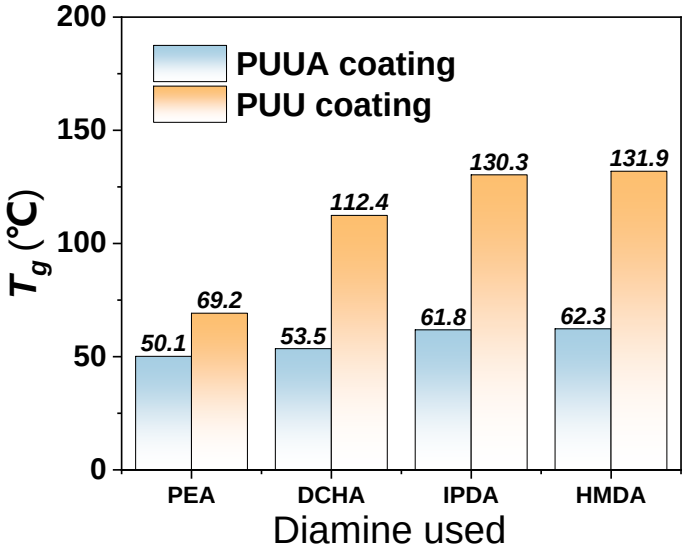


Figure S7. T_g of the PUUAs and PUUs

Table S2. Crosslinking density of the PUUAs and PUUs

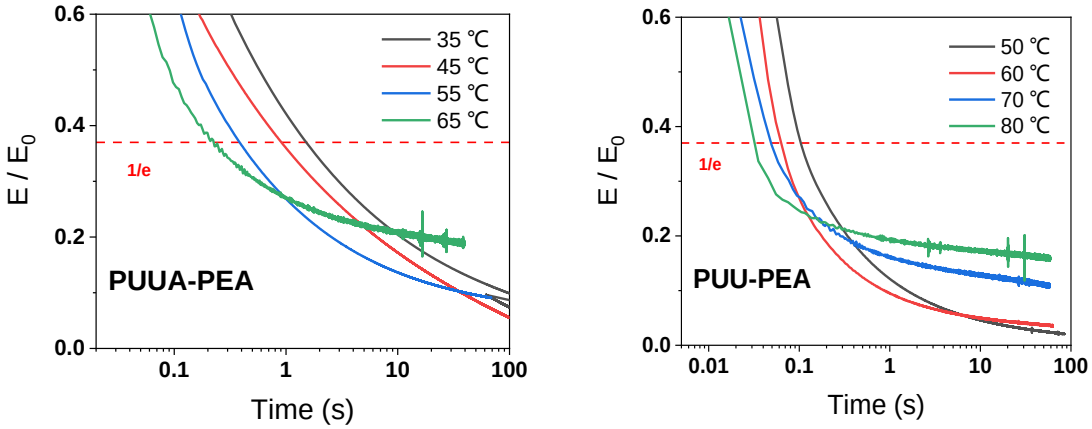
Diamine used	T_g / ℃		υ_e / mol·m^{-3}	
	PUUA	PUU	PUUA	PUU
PEA	50.1	69.2	337.9	169.4
DCHA	53.5	112.4	908.4	198.0
IPDA	61.8	130.3	1071.0	207.6
HMDA	62.3	131.9	791.8	215.5

The empirical formula (Eq. S1) for calculating the crosslink density (υ_e) using the storage modulus of the rubber plateau region obtained by DMA:

$$\upsilon_e = \frac{E_r}{3\mathrm{R}(T_g+30)} \qquad \text{(Eq. S1)}$$

where E_r is the energy storage modulus of the rubber plateau region, Pa; R is the gas constant; T_g is the glass transition temperature, K. The crosslinking density υ_e was obtained in mol·m^{-3}.

Stress relaxation of the PUUAs and PUUs



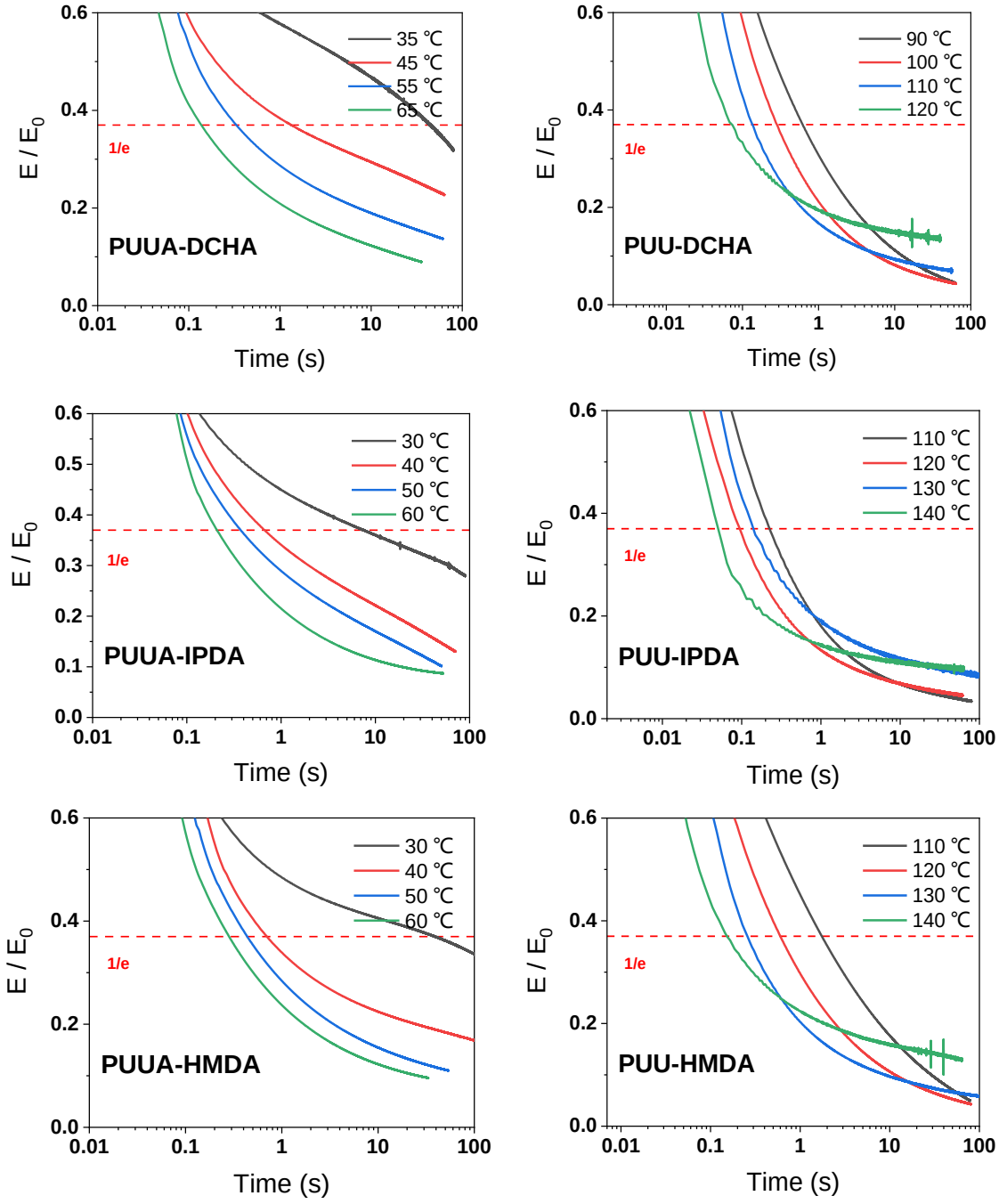


Figure S8. Normalized stress relaxation curves of the PUUAs and PUUs

The relaxation time τ as a function of temperature conforms to the *Arrhenius* equation, and the data obtained in Figure S8 were plotted in terms of ln(τ) against

1000/T . The equation used is given in Eq. S2. Using the slope of the fitted straight line, it is possible to calculate the *Arrhenius* activation energy E_a before and after the post-curing of the PUUAs and PUUs, and thus to explore the transformation curing process.[1, 2]

$$\ln(\tau)=\frac{E_a}{\mathrm{RT}}+\ln(\tau_0) \qquad \text{(Eq. S2)}$$

where τ is the stress relaxation time, E_a is the Arrhenius activation energy, R is the gas constant taken as 8.314, and T is the temperature.

Thermodynamic properties of the PUUAs and PUUs

Table S3. Mechanical parameters of PUUAs and PUUs

Samples	Tensile strength / MPa	Young's modulus / MPa	Elongation at break / %	Toughness / $J \cdot m^{-3}$
PUUA-PEA	6.3 ± 1.6	32.3 ± 9.8	32 ± 6	1.14 ± 0.26
PUU-PEA	11.4 ± 3.2	91.3 ± 32.0	14 ± 4	0.69 ± 0.14
PUUA-DCHA	5.9 ± 0.2	45.9 ± 20.8	21 ± 6	0.77 ± 0.19
PUU-DCHA	4.1 ± 0.6	80.7 ± 10.7	8 ± 1	0.14 ± 0.02
PUUA-IPDA	8.0 ± 0.6	35.8 ± 4.1	27 ± 2	1.14 ± 0.12
PUU-IPDA	3.3 ± 0.4	65.0 ± 18.0	8 ± 1	0.13 ± 0.03
PUUA-HMDA	6.1 ± 0.6	22.0 ± 4.2	40 ± 9	1.41 ± 0.32
PUU-HMDA	10.2 ± 2.0	126.2 ± 27.7	15 ± 5	0.61 ± 0.17

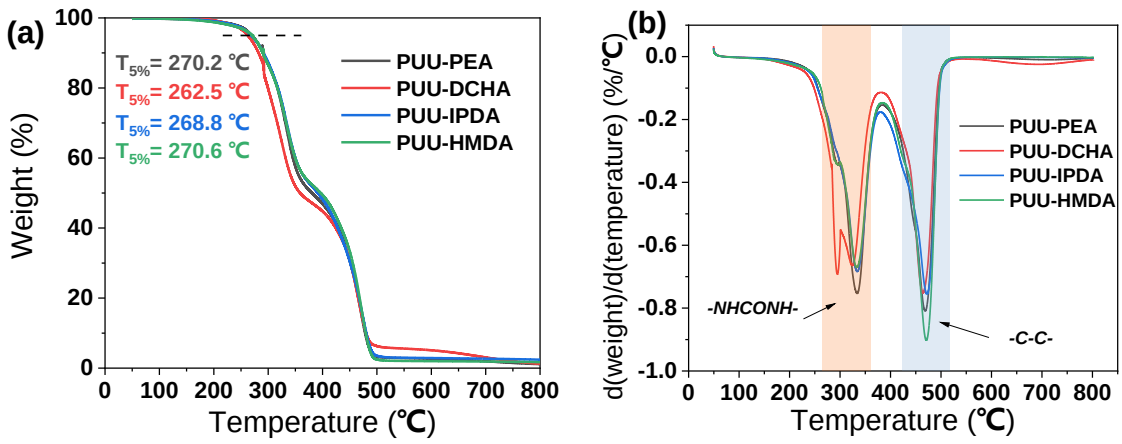
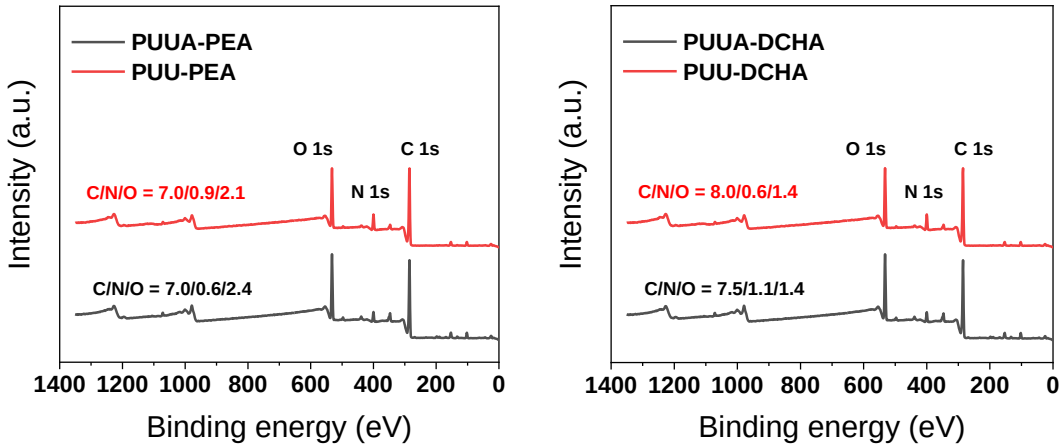


Figure S9. TG and DTG spectra of the PUUs

Coating properties of the PUUAs and PUUs



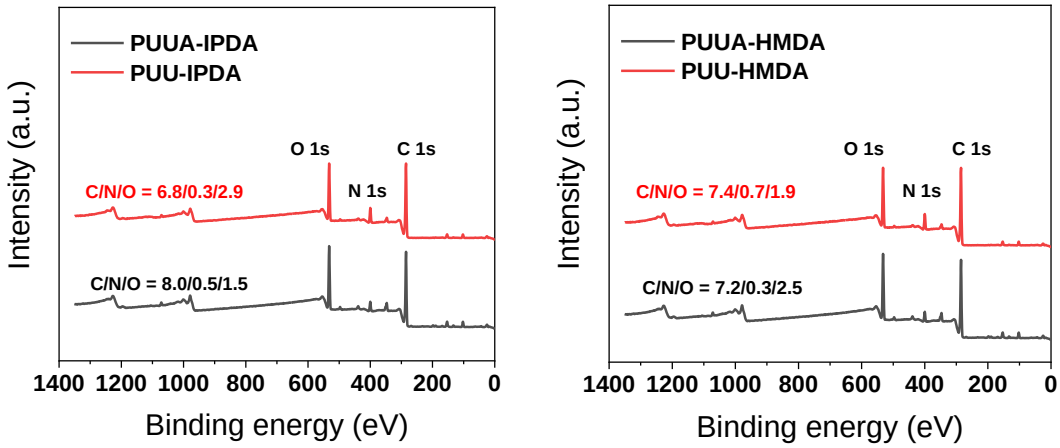


Figure S10. XPS full spectrum of the PUUAs and PUUs

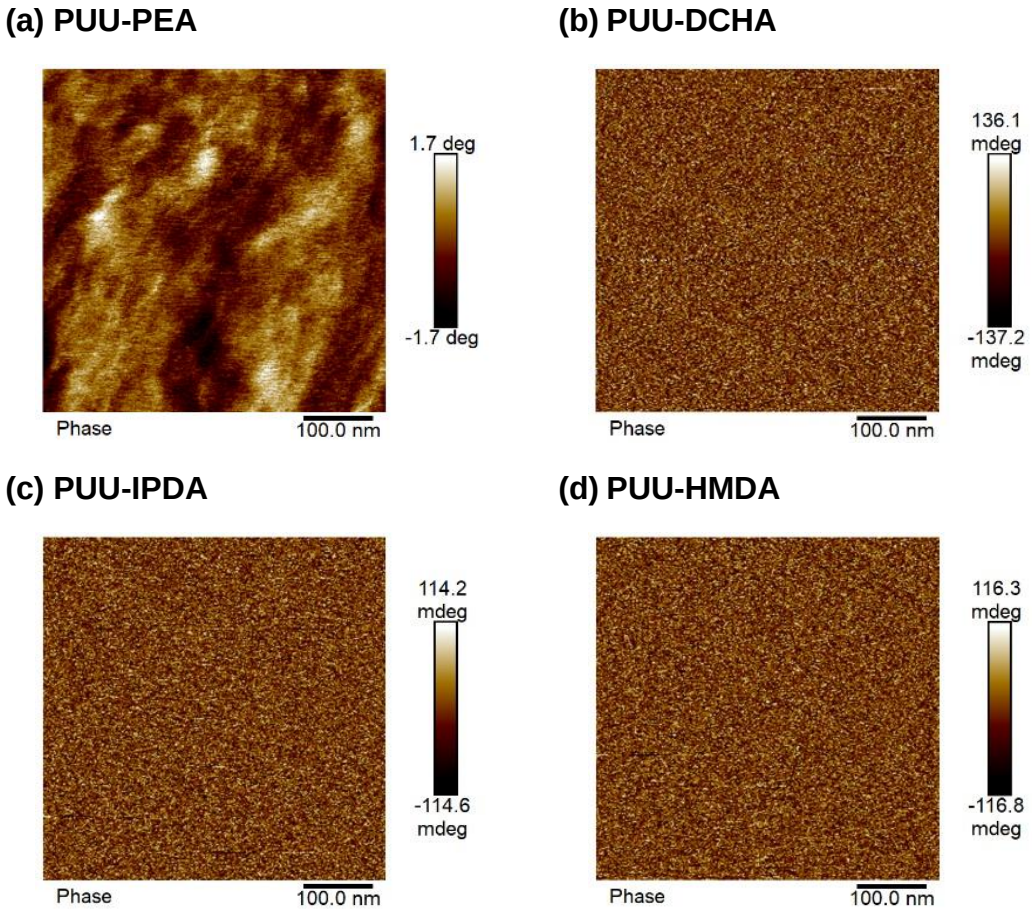


Figure S11. AFM phase diagram (a–d) of the PUU coatings

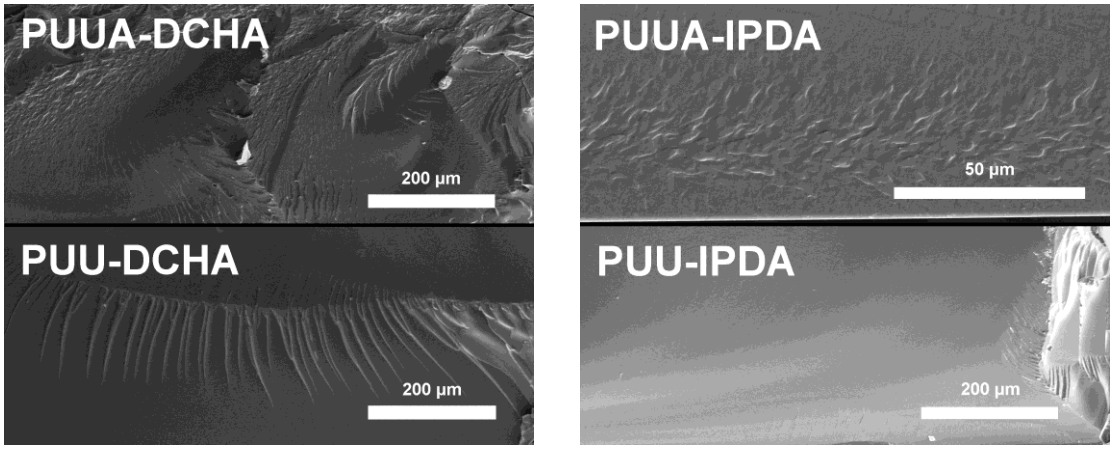


Figure S12. SEM cross-sectional images of PUUA and PUU coatings prepared by DCHA and IPDA

Chemical protection evaluation

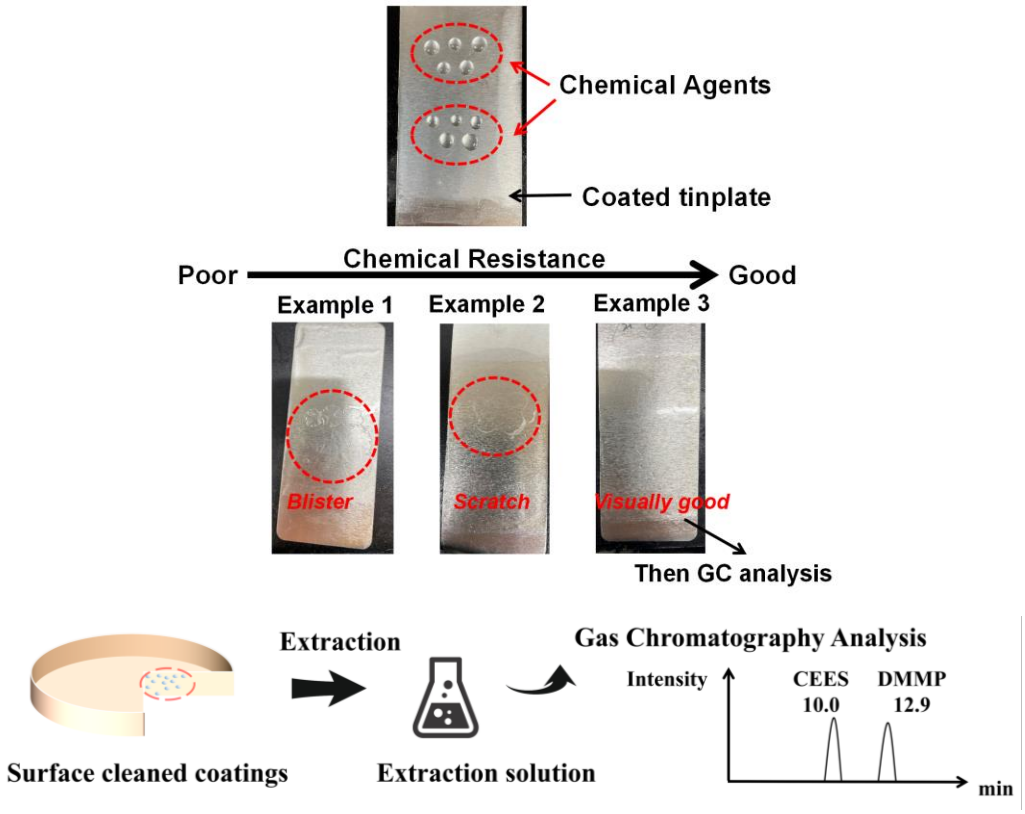


Figure S13. Procedures for assessing chemical defence performance in our research[3, 4]

Table S4. Retention of all PUUAs and PUUs to CEES

Sanples	*Retention* – exposure time / %
	CEES–1h
PUUA-PEA	0.29 ± 0.04
PUUA-DCHA	0.86 ± 0.09
PUUA-IPDA	0.57 ±0.07
PUUA-HMDA	0.66 ± 0.08
PUU-PEA	0
PUU-DCHA	0.19 ± 0.03
PUU-IPDA	0.38 ± 0.05
PUU-HMDA	0.55 ± 0.07

Solvent extraction

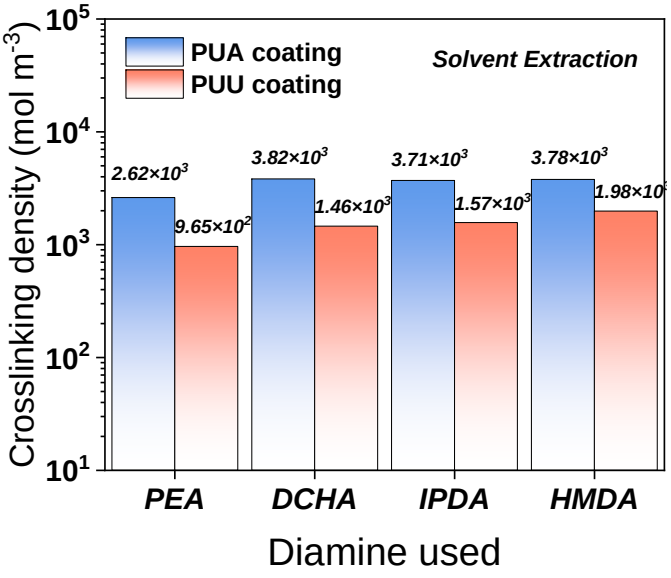


Figure S14. Crosslink density of PUUAs and PUUs measured by the solvent extraction method

A solvent extraction method was also used to measure the crosslink density of

PUUAs before and after heat curing to investigate the accuracy of the crosslink density calculated by DMA. At least 5 g of coating samples were immersed in toluene at 25 °C for 24 h. The mass of the dried samples was weighed after 24 h of oven drying at 80°C. The empirical formula *Flory-Rehner* equation was used for calculation (Eq. S3 and Eq. S4):[5, 6]

$$\upsilon_e = \frac{-(\ln(1-V_r)+V_r+\chi {V_r}^2)}{V_0(V_r^{\frac{1}{3}})} \quad \text{(Eq. S3)}$$

$$V_r = \frac{\frac{m_d}{\rho_2}}{\frac{m_d}{\rho_2}+\frac{m_s-m_d}{\rho_1}} \quad \text{(Eq. S4)}$$

Where, V_r denotes the volume fraction of the sample, m_0 is the original mass of the sample, m_s is the mass of the sample after dissolution, and md the mass of the sample completely dried (md). χ denotes the *Flory-Huggins* polymer-solvent interaction parameter (0.417 for toluene) [6], and V_0 denotes the molar volume of solvent (106.2 $cm^3 \cdot mol^{-1}$ for toluene). ρ_1 denotes the density of the solvent (0.865 $g \cdot mol^{-1}$ for toluene), and ρ_2 denotes the density of the sample (the densities varied little in this paper and were taken to be 1.00 $g \cdot mol^{-1}$).

The proportion of *N-H* bonding was obtained by ratioing the integral area of the *N-H* splitting peaks (398-399 eV) to the integral area of the total *N 1s*.

$$\text{Proportion of } N\text{-}H \text{ bonding per Nitrogen} = \frac{A_{399\ eV}}{A_{\text{total } N\ 1s}} \times 100\% \quad \text{(Eq. S5)}$$

where $A_{399\ eV}$ is the split-peak integral area of the *N-H* bonding, and $A_{total\ N\ 1s}$ is the integral area of the entire N 1s peak.

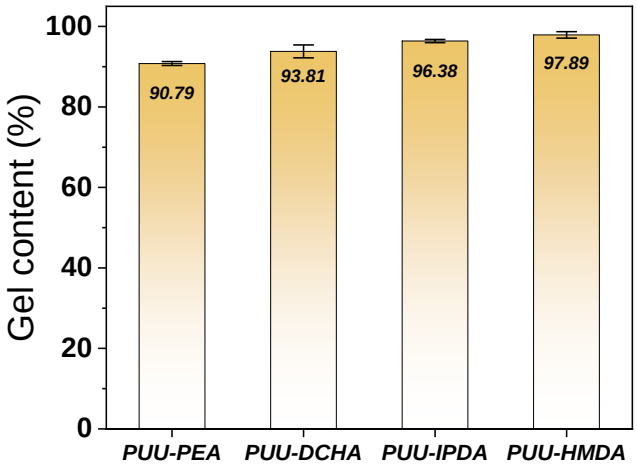


Figure S15. Gel content of PUUs

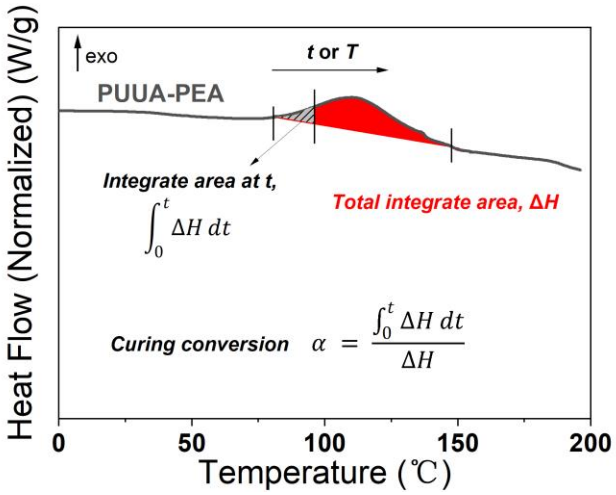


Figure S16. Explanation of the Equation 2 for conversion

(PUUA-PEA as an example)

References

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