

# Supporting Information

## **MOF-based porous liquids towards a highly stressed and chemically resistant fire-safety polyurea elastomer**

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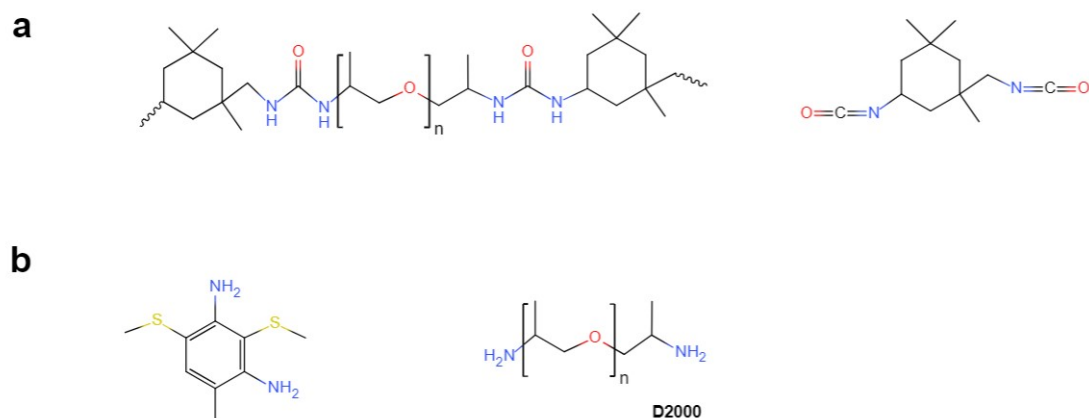
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## 2. Experimental section

### 2.1. Materials



**Fig. S1.** Chemical structure of (a) polyurea component A and (b) polyurea component B.

### 2.5. Preparation of polyurea (PUA) composite

**Table S1.** Formulations of flame-retardant polyurea composite samples.

Sample	Composition (wt.%)						
	Polyurea component A [g]	Polyurea component B [g]	U@PA@OA PL-5 [g]	U@PA@OA PL-10 [g]	U@PA@OA PL-20 [g]	U@PA@OA-PS [g]	U@PA@OA %w/w
	PUA	25.0	25.0				
PUA/U@PA@OA PL-5	25.0	25.0	5.56				0.50
PUA/U@PA@OA PL-10	25.0	25.0		5.56			1.0
PUA/U@PA@OA PL-20	25.0	25.0			5.56		2.0
PUA/U@PA@OA-PS	25.0	25.0				5.56	2.0

### 2.6. Characterization

The morphology of as-prepared samples was characterized by scanning electron microscopy (SEM, Hitachi SU8020, Hitachi Ltd., Tokyo, Japan) and transmission

electron microscopy (TEM, Tecnai G2 F30 S-TWII, FEI, Hillsboro). The carbon-coated formvar film was obtained by Zhongjingkeyi (Beijing) Film Technology Co., Ltd.

X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Scientific K-Alpha X-ray photo-electron spectrometer (Thermo Fisher Scientific) using an Al K $\alpha$  X-ray source.

X-ray powder diffraction (XRD) patterns were taken with an X-ray diffractometer (DX-2600, Rigaku, Tokyo, Japan) at 40 kV and 15 mA using a Cu K $\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) X-ray source at a scanning rate of  $8^\circ$  per min.

Fourier transform infrared (FTIR) spectra was performed on a Tensor 27 IR spectroscopy (Bruker Optics, Germany) to analyze the chemical structure of samples.

The specific surface areas and pore diameter distribution of samples were evaluated on the 3H-2000PS2 analyzer apparatus (BeiShiDe, Beijing), calculated by N<sub>2</sub> sorption isotherms using the Brunauer-Emmett-Teller (BET) method.

Thermogravimetric analysis (TGA) was conducted using a TOLEDO STARE thermal analyzer (Mettler Toledo, Switzerland). All TGA experiments were performed under a N<sub>2</sub> atmosphere from 50-800 °C at a rate of 10 °C/min.

Raman scattering spectra were recorded with a Renishaw inVia confocal Raman microscope system (Renishaw, U.K.) using 532 nm laser source.

The limit oxygen index (LOI) values of PUA composites were evaluated by a FTAIL 1600 LOI instrument (Rheometric Scientific Ltd., Suzhou, China), following to the ASTM D 2863 procedure, with the sample dimensions of  $100 \times 6.5 \times 3 \text{ mm}^3$ . To

ensure reliable results, each group of experiments was repeated three times.

Vertical burning tests were performed using the UL-94 standard on samples of dimensions  $125 \times 13 \times 3.2 \text{ mm}^3$ . To ensure reliable results, each group of experiments was repeated three times.

Cone calorimeter measurements (Cone) were examined on a Fire Testing Technology apparatus (Phoenix Instruments Co, Ltd., Suzhou, China), referring to the ISO 5660 protocol under heat flux of  $50 \text{ kW/m}^2$  (the sample dimensions:  $100 \times 100 \times 3 \text{ mm}^3$ ). The repeatability of cone test results was allowed within  $\pm 10\%$ , and the data for this work was the average of two measurements.

The mechanical properties of PUA composites were conducted on a universal mechanical testing machine (DXLL-5000, Shanghai D & G Measure Instrument Co. Ltd, China) with a drawing speed of  $50 \text{ mm/min}$ , and the results were averaged after three parallel tests for each specimen.

High strain-rate compression tests of PUA and its composites were conducted using a split Hopkinson pressure bar (SHPB) system. Tests were carried out under the different strain rates ( $3000 \text{ s}^{-1}$  and  $6000 \text{ s}^{-1}$ ).

The Rheometer (DHR-2) was utilized to examine the liquid properties.

The gaseous products of PUA composites were analyzed by thermogravimetric analysis–Fourier transform infrared spectroscopy (TG-FTIR) with a Mettler-Toledo thermogravimetric analyzer (Mettler Toledo, Switzerland) coupled with a Tensor 27 FTIR spectrophotometer (Bruker Optics, Germany) under a nitrogen atmosphere from  $50 \text{ }^\circ\text{C}$  to  $900 \text{ }^\circ\text{C}$  at a rate of  $20 \text{ }^\circ\text{C/min}$ .

The contact angle was measured by the pendant drop method with an SL150E instrument (KINO, USA), and water was selected as the standard liquids.

The chemical resistance of the polyurea composite samples was investigated by immersion experiments. About 150 mg of sample was placed in 40 mL of 3.5 wt% NaCl solution, 3.5 wt% HCl aqueous solution, 3.5 wt% NaOH aqueous solution, and deionized water at 50 °C, respectively. After the immersion experiments, the insoluble part was sucked dry and photographed.

The weight loss percentage (*W.L* (%)) of the polyurea composite samples was quantified using **Eq. (1)**.

$$W.L (\%) = \frac{m_1 - m_0}{m_0} \times 100 \quad \text{Eq. (1)}$$

where  $m_0$  and  $m_1$  are the original or final weight of the polyurea composite sample before and after degradation, respectively.

### 3. Results and discussion

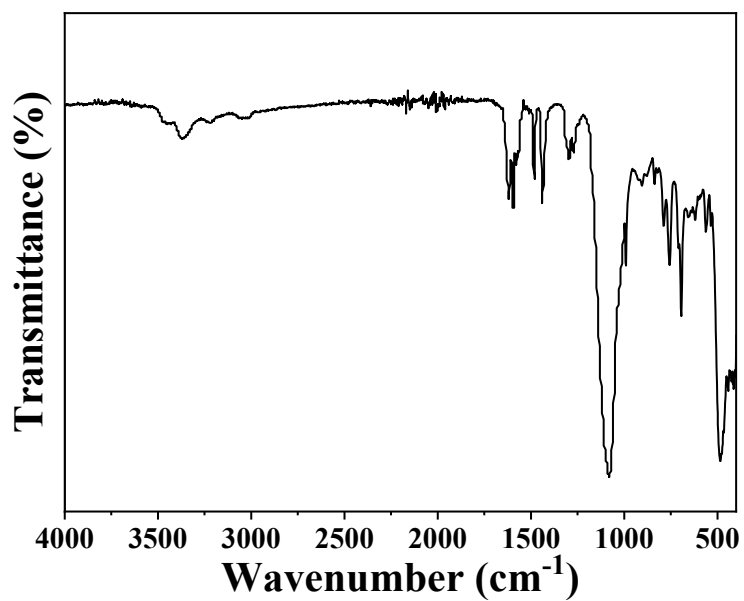


Fig. S2. FTIR spectrum of OAPS.

Table S2. XPS data of the products.

Signal	Binding energy (eV)	Content (Wt.%)		
		UiO-66-NH <sub>2</sub>	U@PA	U@PA@OA
C 1s	285.5	55.57	50.69	49.54
N 1s	398.6	6.37	7.08	7.03
O 1s	529.5	33.64	33.31	33.68
Zr 3d	182.9	4.42	4.85	4.03
P 2p	133.4	/	4.07	2.91
Si 2p	102.6	/		2.81

**Table S3.** TGA and DTG data of the products under nitrogen.

Samples	$T_{5\%}$ (°C)	$T_{max}$ (°C)	Residues at 800 °C (%)
UiO-66-NH <sub>2</sub>	248.6	306.2 & 400.2 & 557.0	56.8
U@PA	252.7	432.7 & 545.7	69.5
U@PA@OA	254.8	430.6 & 542.8	71.2

**Table S4** BET surface area and average pore diameter data of the products.

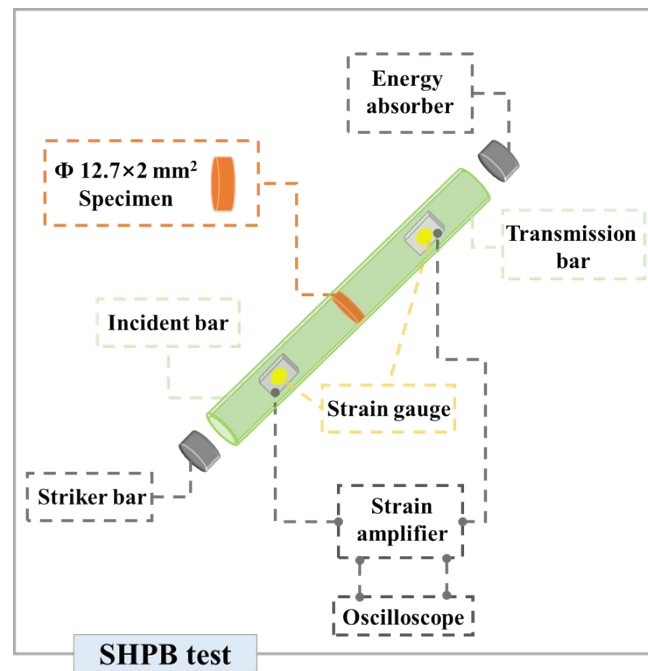
Samples	$S_{BET}$ (m <sup>2</sup> /g)	Average pore diameter (nm)
UiO-66-NH <sub>2</sub>	875.3	1.1
U@PA	433.2	6.8
U@PA@OA	397.6	6.1

**Table S5.** TGA and DTG data of U@PA@OA PLs and PDMS under nitrogen.

Samples	$T_{5\%}$ (°C)	$T_{max}$ (°C)	Residues at 800 °C (%)
U@PA@OA PL-5	351.2	614.1	6.2
U@PA@OA PL-10	352.1	620.8	8.5
U@PA@OA PL-20	353.4	624.0	18.8
PDMS	346.5	464.7	4.0

**Table S6.** Tensile strength as well as elongation at break of PUA and its composites.

Samples	Tensile strength (MPa)	Elongation at break (%)
PUA	24.7±0.8	290.1±11.3
PUA/U@PA@OA PL-5	26.6±0.6	298.1±12.5
PUA/U@PA@OA PL-10	28.4±0.7	324.5±10.8
PUA/U@PA@OA PL-20	32.9±0.6	339.8±10.4
PUA/PDMS	22.4±0.7	276.3±11.2
PUA/U@PA@OA-PS	22.8±0.8	237.7±10.9



**Fig. S3.** Schematic diagram of split Hopkinson pressure bar (SHPB) system.



**Table S7.** TGA and DTG data of the PUA and its composites under nitrogen.

Samples	$T_{5\%}$ (°C)	$T_{max}$ (°C)	Residues at 800 °C (%)
		( $T_{max1}$ & $T_{max2}$ & $T_{max3}$ )	
PUA	248.3	282.4 & 422.8	5.7
PUA/U@PA@OA PL-5	229.5	281.3 & 411.7 & 628.2	8.7
PUA/U@PA@OA PL-10	226.3	282.5 & 412.3 & 633.2	9.6
PUA/U@PA@OA PL-20	224.0	281.9 & 412.9 & 635.2	13.3
PUA/U@PA@OA-PS	228.5	280.5 & 411.1 & 627.8	11.0
PUA/PDMS	237.0	277.5 & 411.3 & 567.1	7.3

**Table S8.** LOI values, UL-94 rating, and cone calorimeter data for PUA and its composites.

Items	PUA	PUA/U@PA@O A PL-5	PUA/U@PA@OA PL-10	PUA/U@PA@OA PL-20	PUA/PDMS	PUA/U@PA@OA-PS
LOI (%)	22.2	24.4	25.0	<b>26.9</b>	23.3	25.6
UL-94 rating	V-2	V-2	V-2	<b>V-0</b>	V-2	V-2
pHRR (kW/m <sup>2</sup> )	1150.1	640.1	654.7	<b>532.5</b>	803.8	548.2
THR (MJ/m <sup>2</sup> ) (500 s)	89.8	79.4	74.1	<b>56.9</b>	82.1	67.4
TSP (m <sup>2</sup> ) (500 s)	15.3	11.8	11.3	<b>10.1</b>	12.8	11.0
av-COY (kg/kg)	0.0640	0.0489	0.0441	<b>0.0358</b>	0.0502	0.0427
av-CO <sub>2</sub> Y (kg/kg)	1.7135	1.6652	1.6444	<b>1.5765</b>	1.6925	1.6171
Char Residue (wt%)	3.8	9.7	10.9	<b>13.8</b>	8.8	12.0

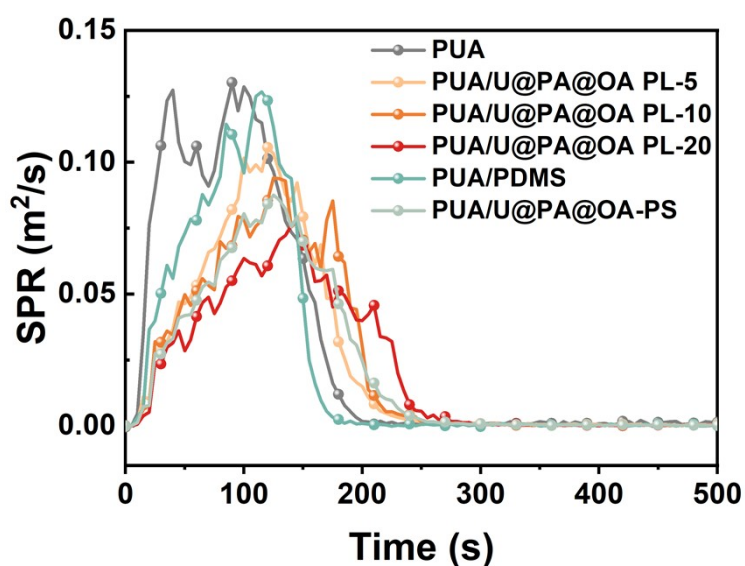


Fig. S4. SPR curves of PUA and its composites.

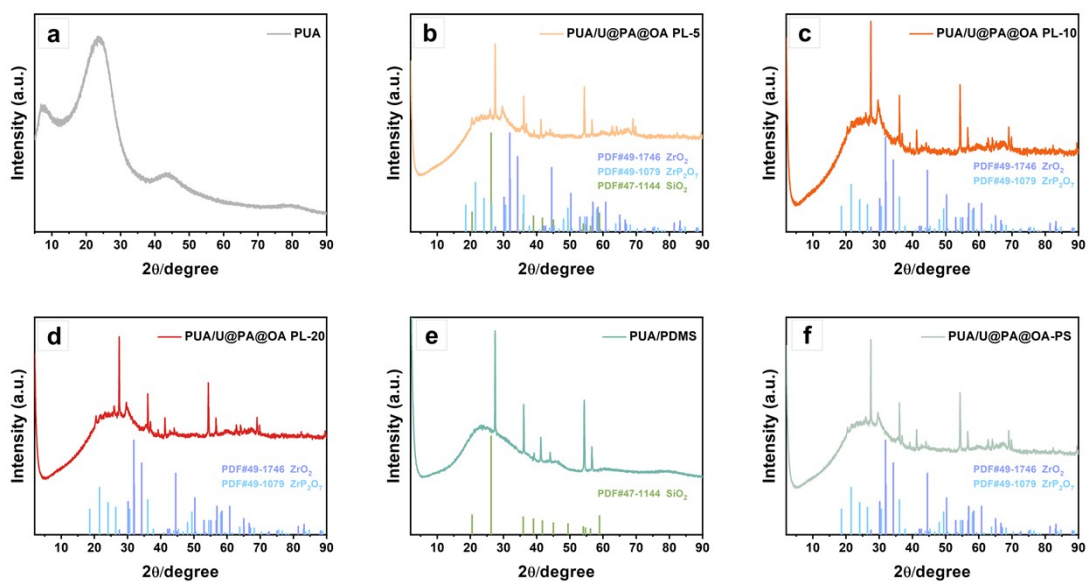
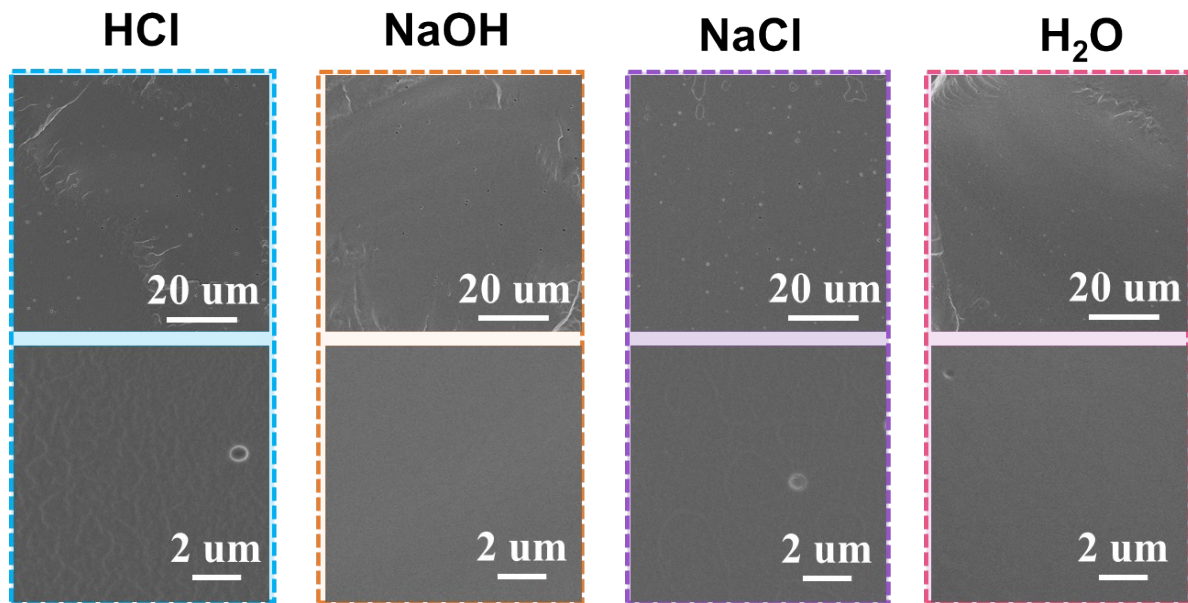


Fig. S5. XRD patterns of char residues after Cone tests from PUA and its composites.



**Fig. S6.** SEM images and enlarged SEM images of PUA brittle section after 60 days of the chemical resistance test.