Electronic Supplementary Information

Strippable Catechol-terminated Polyurethane Coating for Large-area Radioactive Cesium Decontamination

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Supplementary Notes

Materials

Dopamine hydrochloride, *N, N*-dimethylformamide (DMF), molecular sieves, 4 Å (zeolite) were purchased from Sigma-Aldrich. Polycaprolactone diol (PCL, average M.N. 2000), Triethylamine (TEA) were procured from Thermo Scientific Chemicals. 1,3-bis(isocyanatomethyl)cyclohexane (H_6XDI) was obtained at Hanwha Solutions (Seoul, Korea). Dibutyltin dilaurate (DBTDL) was purchased from TCI Chemicals. Ethanol was purchased from OCI (Seoul, South Korea). 2-Butanone (MEK), Cesium chloride were sourced from Samchun (Seoul, South Korea). Acetone was purchased from SK Chemicals (Seoul, South Korea). The commercial Decongel™ was acquired from CBI Polymers Inc. (Honolulu, USA), Deionized water (18.2 MΩ·cm at 25 ℃) was used for all the experiments. All reagents were used without further purification.

Synthesis of catechol terminated polyurethane

We reported a facile method to prepare catechol terminated polyurethane by two-step polymerization as illustrated in Figure S1. PCL was dried under vacuum at 60 ℃ for 12 hours. Dry PCL (10 g, 5 mol) and H_6XDI (1.020 g, 5.25 mol) were added to a reactor, DBTDL in MEK (100 ppm) was added as a catalyst, and the mixture was stirred for 4 hours at 60 ℃ under nitrogen. Dopamine hydrochloride (0.047 g, 0.25 mol) in 2 mL DMF was purged under nitrogen for 30 min and TEA was used to neutralize the hydrochloric acid. Neutralized dopamine hydrochloride was added to a reactor, and the mixture was stirred for 1 hour at 60 ℃ under nitrogen. The final product was obtained by separation and precipitation in methanol and dried under vacuum for 12 hours. Alkyl terminated polyurethane was also synthesized following the same method, except that ethanol was replaced by neutralized dopamine hydrochloride. The structures of the synthesized polymers were analyzed using FT-IR spectroscopy (Figure 2b), and ^{1}H NMR (Figure S2, S3). FT-IR was performed on JASCO FT/IR-4600 (JASCO, Japan) with ATR (Attenuated Total Reflection) accessory. Proton nuclear magnetic resonance (^{1}H NMR) spectra was obtained using 400 MHz NMR spectrometer (AVANCE III HD, Bruker, USA) with CDCl3 as the solvent.

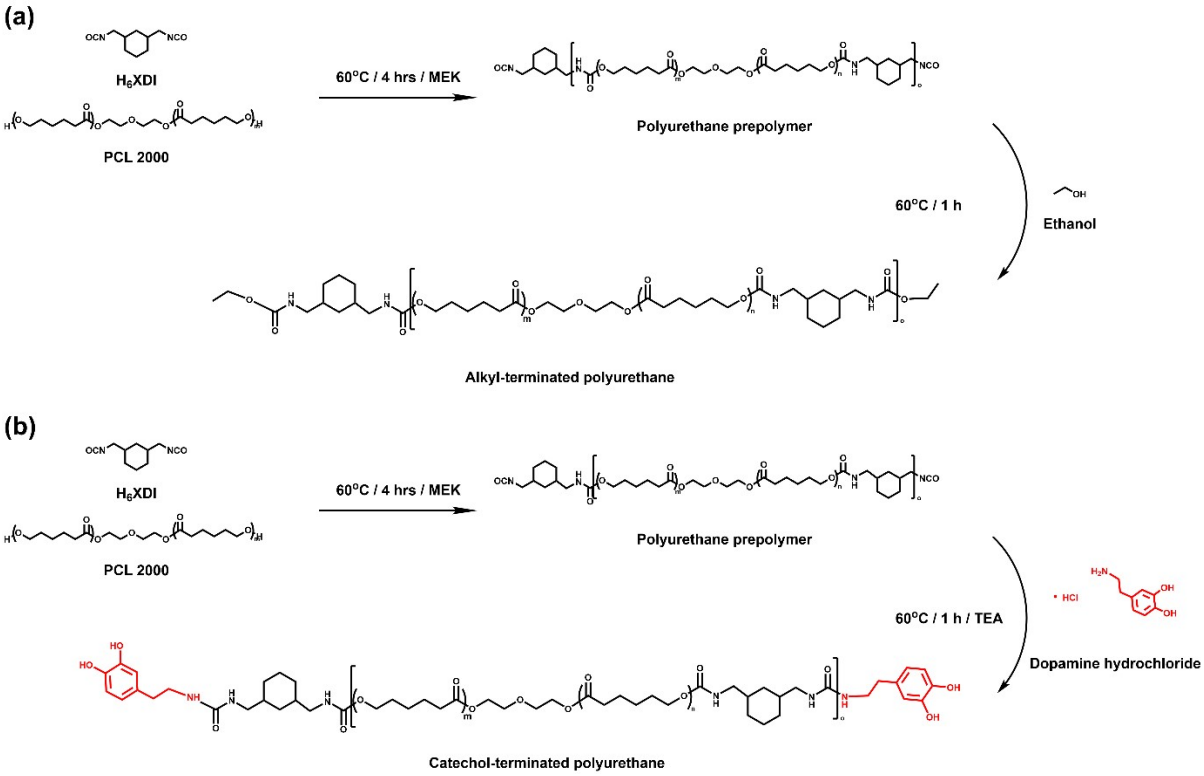

Figure S1. Polymerization of a) alkyl- and b) catechol-terminated polyurethane

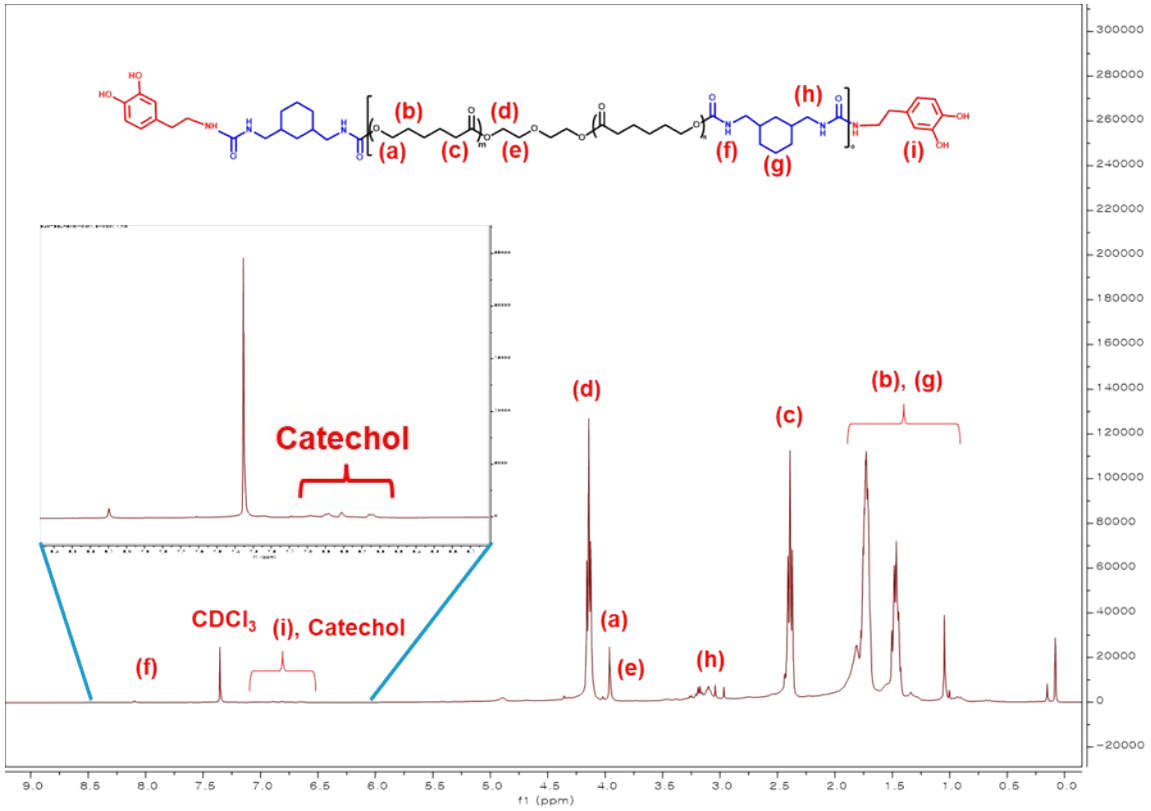

Figure S2. ^{1}H-NMR spectrum of CPU

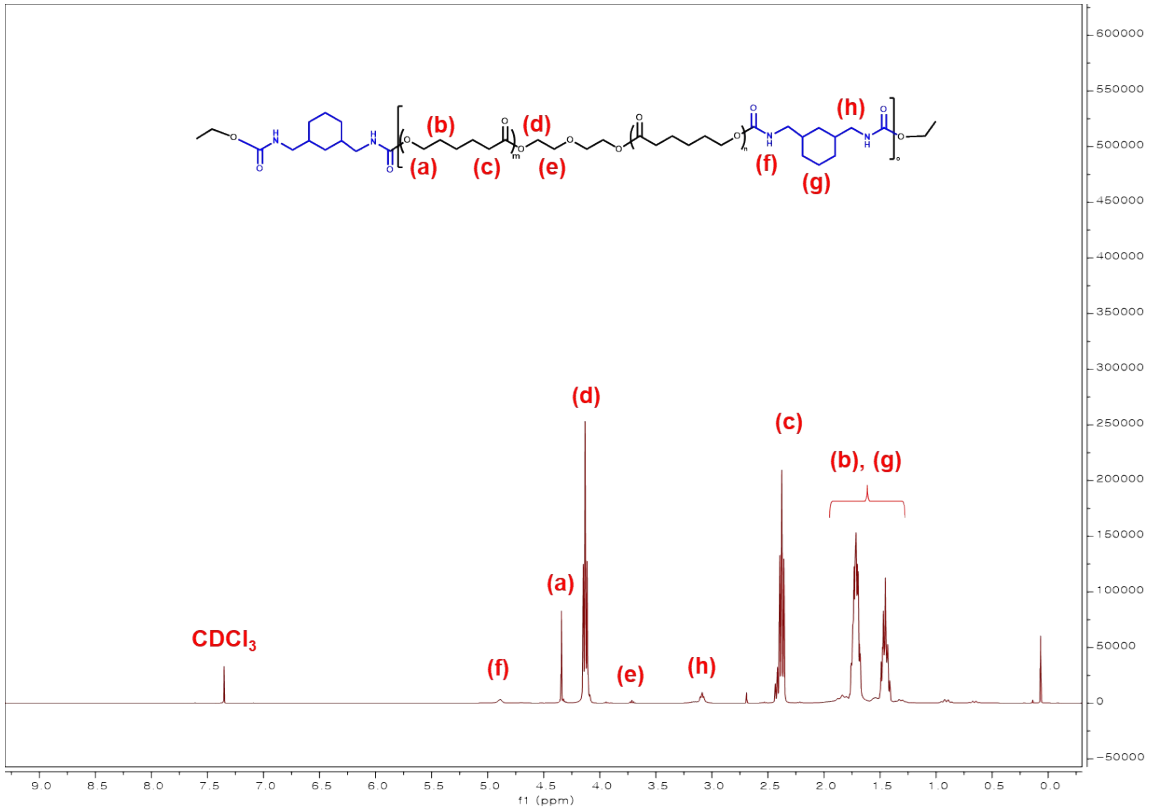

Figure S3. ^{1}H-NMR spectrum of APU

Preparation of strippable polyurethane coatings for characterization

Synthesized polyurethanes (2 g) were dissolved in acetone and water mixture. The mixture was blended using a vortex mixer. The final product was coated on a PET film (SG31) using a knife coating device (KP-3000VH, KIPAE, South Korea). The coated film was dried for 1 hour. The final thickness of the product was measured to be 100 ± 10 μm. The tensile test was performed using a UTM (WL2100C, Withlab, South Korea) with a crosshead speed of 100 mm min^{-1} at room temperature. The melting temperature (T_m) was estimated by the DSC (Q200, TA Instrument, USA). The specimens (10 mg) were heated from -50 to 100 ℃ with a scanning rate of 10 ℃ min^{-1} under nitrogen protection. The glass transition temperature (T_g) was estimated by DMA (Q800, TA Instrument, USA). Thermal stability was estimated by TGA (Q400, TA Instrument, USA). The specimens were heated from 30 to 600 ℃ with a heating rate of 10 ℃ min^{-1} under nitrogen atmosphere. The molecular weight of the polyurethane was measured by GPC (1260 Infinity II LC, Agilent technologies) (Table S4). In the case of molecular weight measurement, only alkyl-terminated polyurethane polymer was measured to avoid inaccurate results due to catechol moiety. The concentration of sample was 3.0 mg mL^{-1} in tetrahydrofuran (THF, 99.9%, HPLC grade, Samchun). GPC measurements were carried out using THF as eluent with a flow rate of 1.0 mL min^{-1}. All samples were calibrated by polystyrene standards.

Adhesive properties test

The peel strength test and lap shear test were performed using a UTM (WL2100C, Withlab, South Korea). To examine the 180° peel adhesion test, polyurethane coating solution was poured onto a stainless steel (SUS) substrates and dried at room temperature for 3 hrs. After drying, top surface of the coating was attached to an adhesive backing film made of custom-built PSA[1] with polyethylene terephthalate (PET) film of 50 μm thickness, which prevented elongation of the coating along the peeling direction. The coating with backing film was pressed twice with a 2.5 kg hand-roller at a speed of 10 mm s^{-1} and then allowed to dwell at room temperature for 15 minutes before the peel adhesion test. The peel strength was measured at a crosshead speed of 300 mm min^{-1} at an angle of 180° at room temperature. For the lap shear test, polyurethane coating solution was poured onto SUS substrate (25.4 × 12.7 mm^2).

Another SUS substrate was placed on top of the coating and there was 50 μm gap between two SUS. The sample was dried for 24 hours at room temperature. The lap shear test was conducted at a crosshead speed of 1.3 mm min^{-1} at room temperature. All the final results were determined to be an average of at least five repetitions.

Performance of CPU and APU in ^{137}Cs removal

^{137}Cs-contaminated porous and nonporous surfaces were prepared by dropping and evaporating a known amount of a ^{137}Cs solution (Eckert & Ziegler) onto SUS or cement (Onuri Maxton Co. Ltd., South Korea) deposited on planchets with a diameter of 4 cm.[2] 2 g of coating solution was applied onto the ^{137}Cs-contaminated surfaces. After 1 hour, dried coating was peeled off of the surface. The radioactivities of the surfaces before and after decontamination were measured using using a HPGe detector (Canberra, USA). and expressed in counts per minute (cpm). The removal efficiency (R) was calculated to evaluate the performance levels of the surface decontaminants using the following equations:

$$R = \frac{A_0 - A_f}{A_0} \times 100\% \quad [2]$$

Where A_0 and A_f represent the initial and final ^{137}Cs activities of the surface, respectively. The experiments were repeated, and the average values were used for analysis. these experiments were duplicated, and the average values were taken for data analysis. The difference between the duplicate values was within ± 5%. A control experiment was performed by using 2 g of commercial strippable coating (DeconGel).

SEM microscopy

SEM images were obtained using SU8220 Cold FE-SEM (Hitachi High-Technologies) to examine the contamination residue. Contaminated surfaces were prepared by sprinkling non-radioactive powder, including Si, Cs, Sr, and Co, followed by dropping and evaporating water

on 1 × 1 cm^2 of SUS. The coating solution was applied onto half of the contaminated surfaces. After 3 hours, the dried coatings were stripped off and the samples were imaged under high vacuum at 10 kV, with 10 mm working distance.

UV-vis spectroscopy

The hydrophilic metal removal efficiency of the polyurethane coatings was evaluated by UV-Vis spectroscopy (V-750, JASCO, Japan). Initial contaminated solution was prepared by mixing 10 mg of non-radioactive contaminants in 50 ml of deionized water. Samples of UV-Vis spectroscopy were prepared as follows: 10 mg of contaminants were sprinkled onto 20 cm^2 of SUS substrate, and 6 mL of deionized water was poured over the contaminated area of substrate to ensure uniform distribution. The well-distributed contaminated area was formed after drying for 3 hours at 100 ℃. The coating solution was poured onto the contaminated area and dried for 1 hour at room temperature. After decontamination, the coating-treated area was soaked in 50 mL of deionized water. The soaking water and initial contaminated solution were tested by UV-Vis spectroscopy. The absorbance at 200 nm was used as a reference and the absorbance spectra of the soaking water and initial contaminated solution were recorded in the wavelength range 200–500 nm. Concentrations of elements were analyzed by ICP-TQ-MS (Nexion 5000, Perkin Elmer, USA).

X-ray photoelectron spectroscopy (XPS)

XPS spectra were obtained using K-alpha (ThermoFisher, USA). CsCl solution of 10 mg mL^{-1} was dropped onto a SUS substrate and evaporated. Then, the APU or CPU solution was applied onto the SUS substrate. After 1 hour, the dried coating was stripped off and the surface in contact with the substrate was analyzed. Pristine samples were prepared without deposition of a CsCl solution. The binding energy scale was calibrated using the high-resolution aliphatic C 1s peak at 285.0 eV.

Dissolution and filtering test

2 g of the strippable coating solution was applied to a contaminated area containing 10 mg of

simulated contaminants. After stripping, the removed coating was dissolved in 10 wt% H_2O solvent and sonicated for 3 hours. This unfiltered solution was filtered using a 0.8 μm syringe filter. Then, 100 mg of zeolite was added to the filtration, followed by filtration using the 0.8 μm syringe filter. After two filtration steps, the final solution was obtained. The Cs^+ concentration at each step was analyzed by ICP-TQ-MS. The waste mass reduction factor (R_m) was calculated using the following equations:

$$R_m = \frac{m_2}{m_1 + m_2} \times 100\%$$

Where m_1 and m_2 represent the mass of dissolved coating and SFO eliminated by coating, respectively.

Spray test using commercial spray equipment

40 g of coating solution were prepared and sprayed onto 20 × 20 cm^2 SUS or cement surface by conventional spray gun (Model LPH-50-102G, Anest Iwata Corporation, Japan) with a nozzle size of 1.0 mm supplied with portable air compressor (Universal Pump 18V, Bosch, Germany).

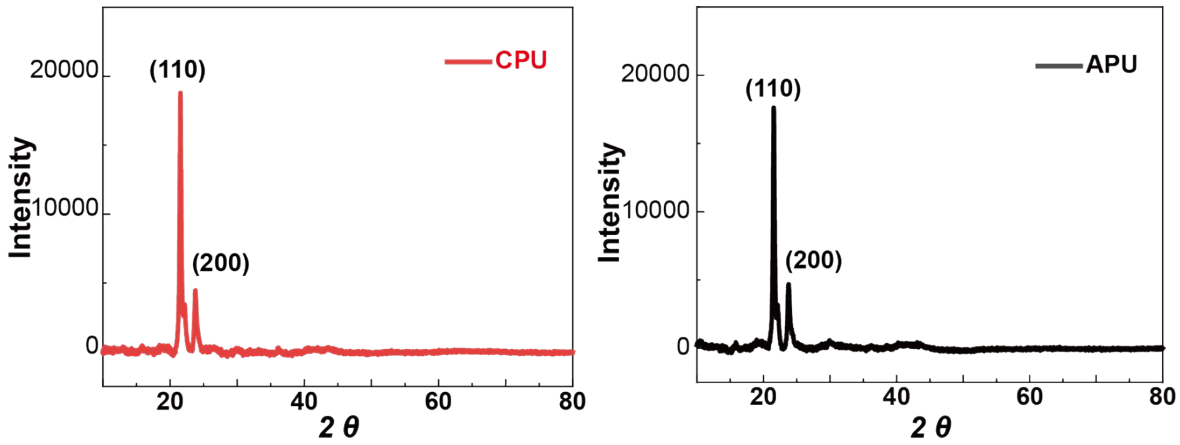

Figure S4. Normal x-ray diffraction patterns of CPU and APU

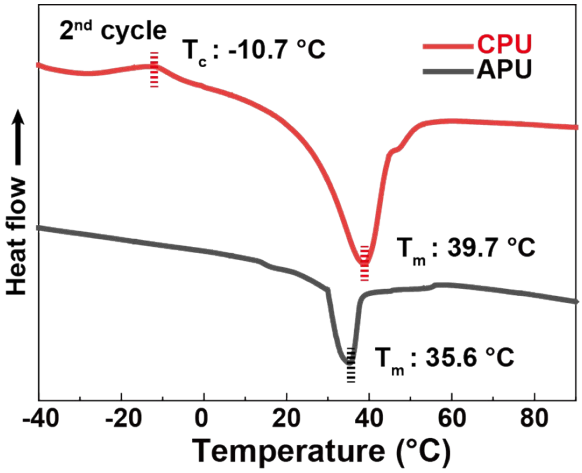

Figure S5. DSC thermograms showing crystallization temperature (T_c) and melting temperatures (T_m) of CPU and APU

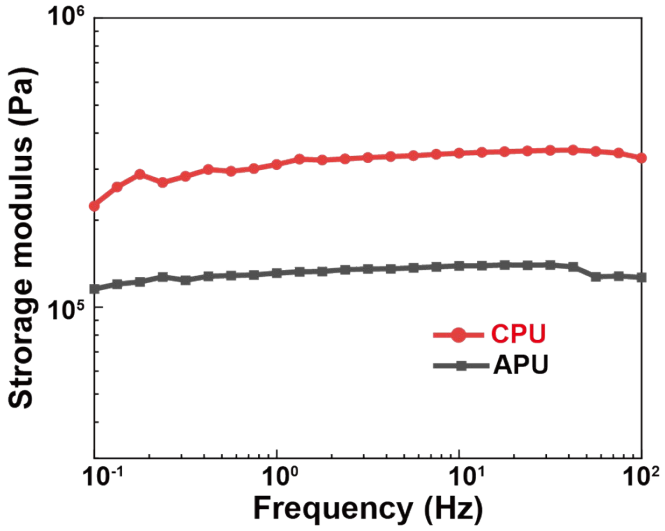

Figure S6. Storage modulus of CPU and APU using rheometer

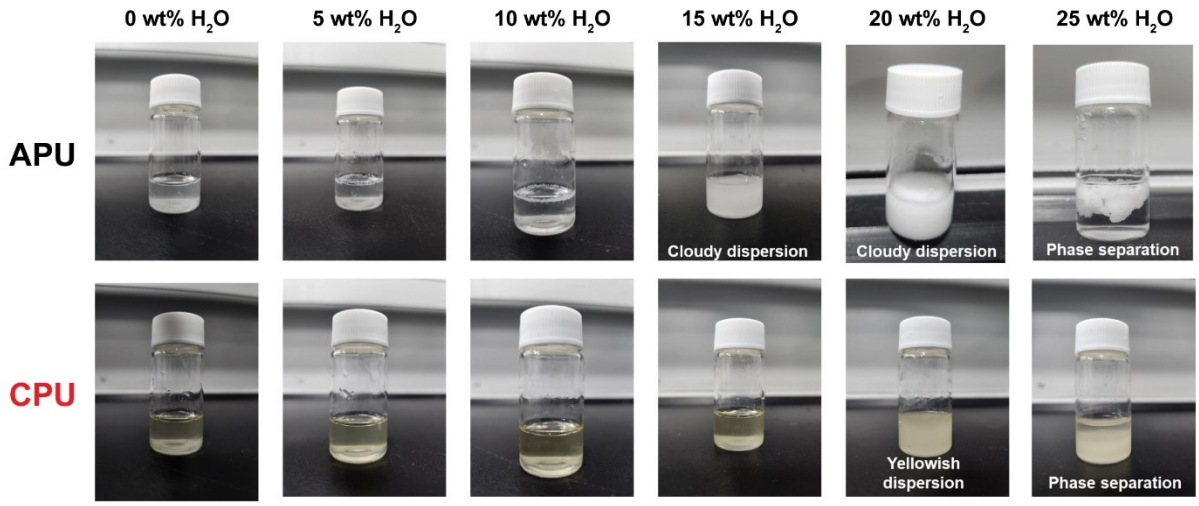

Figure S7. Image of phase separation behavior varying with different water contents in CPU and APU

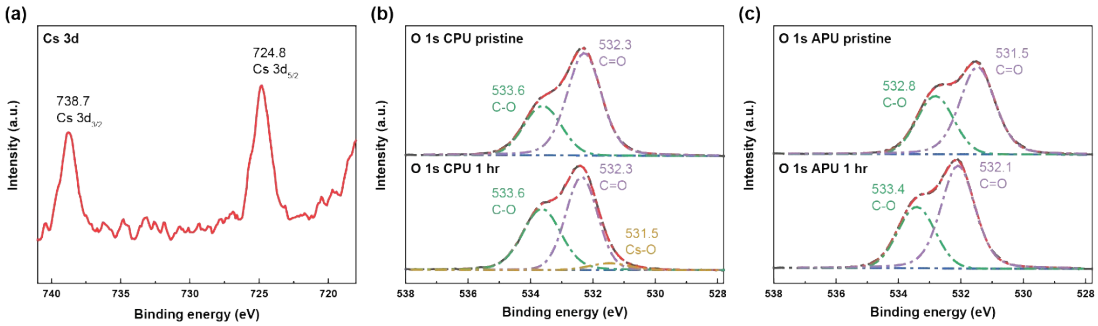

Figure S8. X-ray photoelectron spectroscopy (XPS) spectra. (a) Cs 3d high-resolution XPS spectrum after decontamination. (b) O 1s high-resolution XPS spectra of CPU, and (c) APU.

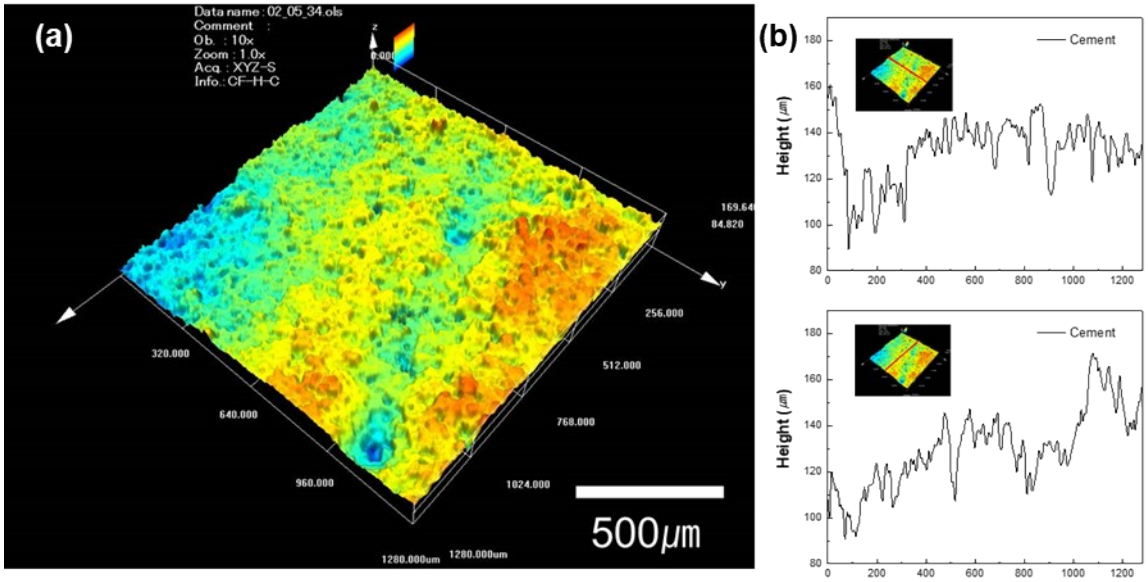

Figure S9. a) 3D surface morphology, and b) profile images of cement obtained by a confocal optical profiler

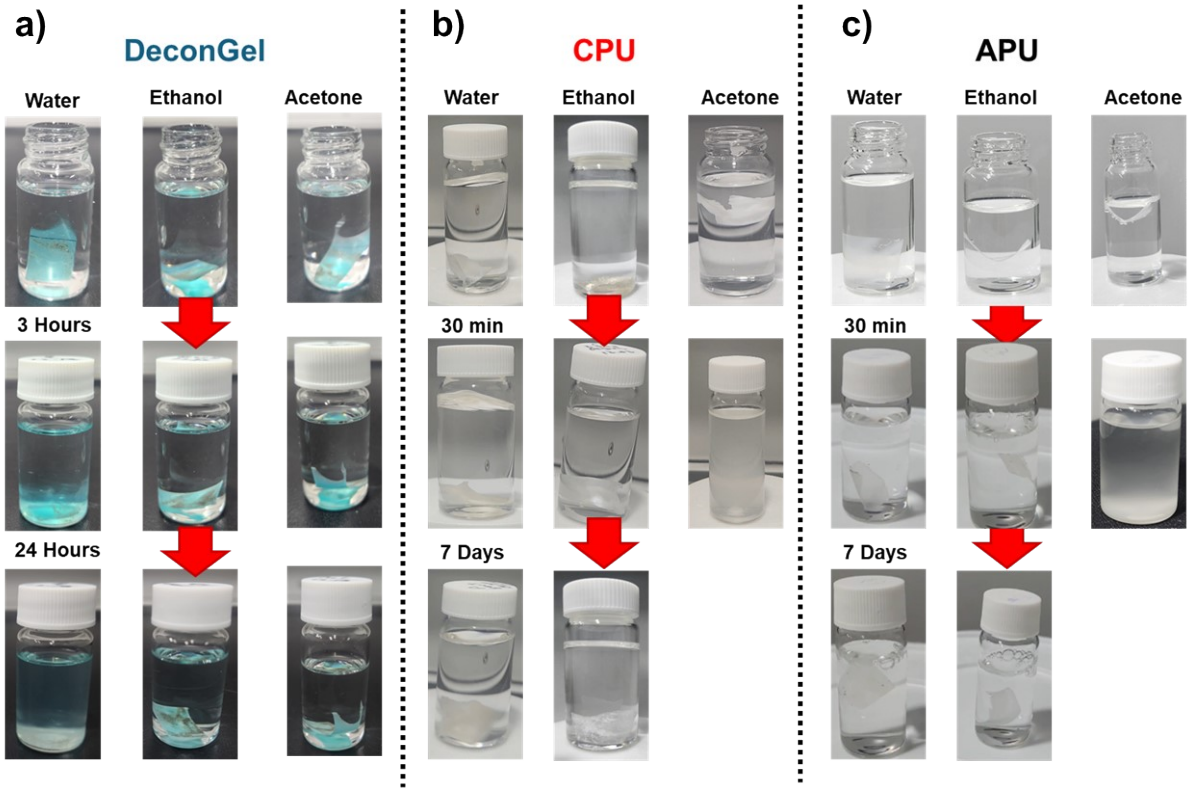

Figure S10. Dissolution behaviors of a) DeconGel, b) CPU, and c) APU

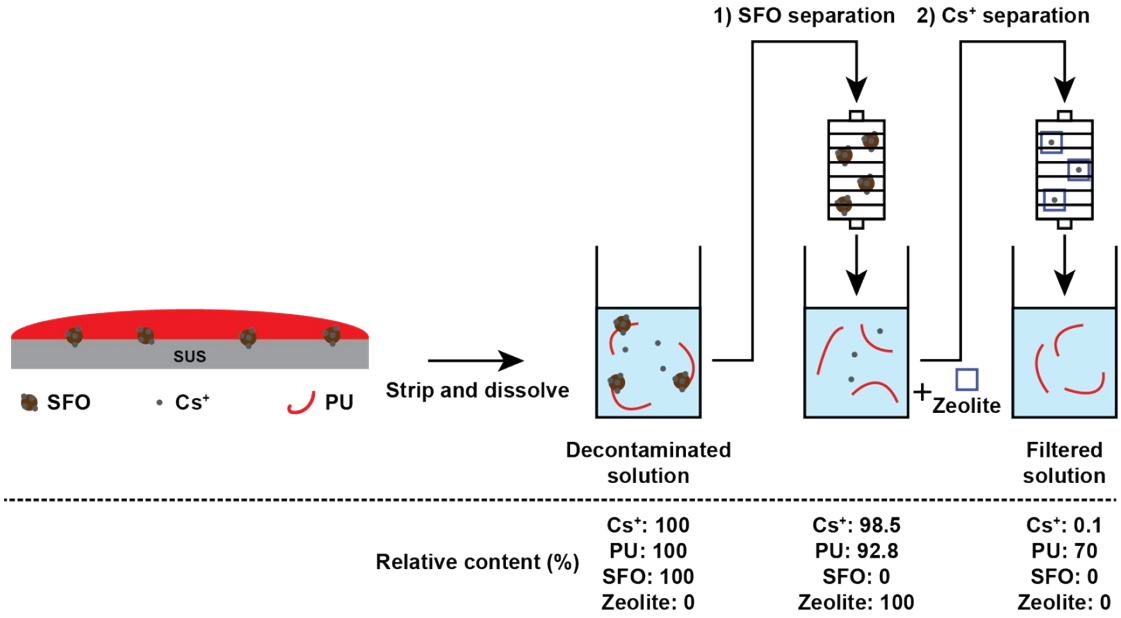

Figure S11. Schematic diagram illustrating the separation and recycling process.

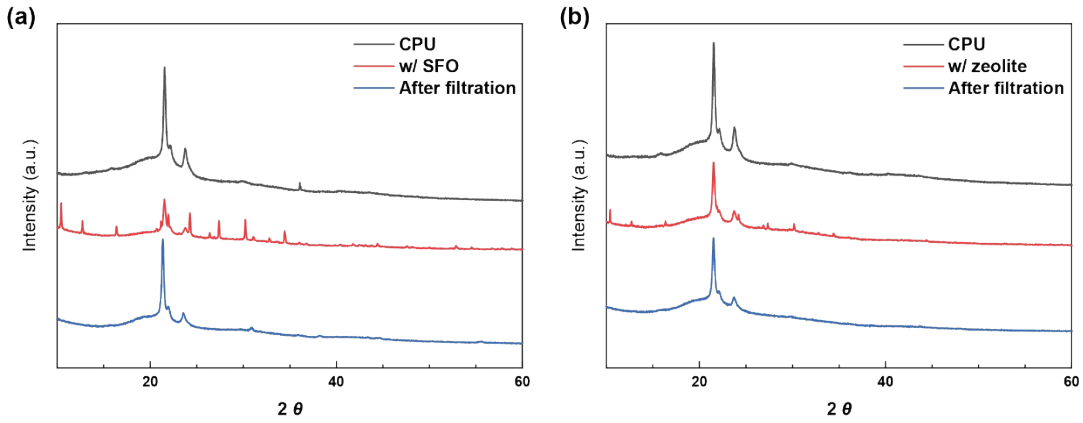

Figure S12. X-ray diffraction patterns of CPU during the separation process, containing (a) SFO and (b) zeolite.

Table S1. Thermal properties of polyurethane coatings

Polymer	T_c [℃]	T_m [℃]	T_{5d} [℃]
CPU	-10.7	39.7	318
APU	-	35.6	240

Table S2. Composition of 5 – 20 wt% CPU samples

SAMPLE	H_2O [g]	Acetone [g]	Polymer [g]
5 wt% CPU	2	10	0.5
10 wt% CPU	2	10	1
15 wt% CPU	2	10	1.5
20 wt% CPU	2	10	2.0

Table S3. Composition of 0 – 25 wt% H_2O samples

SAMPLE	H_2O [g]	Acetone [g]	Polymer [g]
0 wt% H_2O	0	10	2
5 wt% H_2O	0.5	10	2
10 wt% H_2O	1.0	10	2
15 wt% H_2O	1.5	10	2
20 wt% H_2O	2.0	10	2
25 wt% H_2O	2.5	10	2

Table S4. Molecular weights and PDI of NCO/OH 1:1 – 1.15:1 sample

NCO/OH	M.n. [g/mol]	M.w. [g/mol]	PDI	DP (degree of polymerization)
1:1	35,366	66,075	1.87	16.1
1.05:1	32,351	58,906	1.821	14.8
1.10:1	20,890	39,525	1.892	9.5
1.15:1	12,006	21,478	1.789	5.5

Table S5. Feed contents of NCO/OH 1:1 – 1.15:1 sample

Polymer	PCL [mol]	H_6XDI [mol]	Catechol [mol]	TEA [mol]
NCO/OH 1:1	5	5	0	0
NCO/OH 1:1.05	5	5.25	0.50	0.50
NCO/OH 1:1.10	5	5.5	1.00	1.00
NCO/OH 1:1.15	5	5.75	1.50	1.50

Table S6. Mechanical and adhesion properties of polyurethane coatings

	3 hrs CPU	3 hrs APU
Toughness [MJ/m^3]	75.1 ± 2.4	70.7 ± 4.0
Ultimate tensile strength [MPa]	12.2 ± 1.9	9.0 ± 1.5
Elongation at break [%]	847 ± 94	1,230 ± 83
180° Peel adhesion [N/25mm]	17.8 ± 1.4	0.4 ± 0.1
Lap shear adhesion [kPa)	15.7 ± 1.4	~ 0.1

Table S7. Decontamination performances of strippable coatings measuring UV-Vis

Methods	CPU	APU	DeconGel
1 hr drying [%]	90.3	83.7	-
3 hrs drying [%]	97.5	94.7	-
24 hrs drying [%]	-	-	88.4

Table S8. Removal efficiency of ionized heavy metal in 3 hrs CPU and 3 hrs APU measured by ICP-TQ-MS

	Cs [%]	Sr [%]	Co [%]
3 hrs APU	97.0	95.2	86.6
3 hrs CPU	98.4	98.9	97.2
24 hrs DeconGel	96.6	96.2	91.1

Table S9. Viscosity behavior of polyurethane coatings in different shear rates

	Shear rate [s^{-1}]		
	0.1 (Storage)	**100 (Process)**	**1000 (Application)**
APU [Pa s]	2.03	0.85	0.76
CPU [Pa s]	4.85	0.86	0.78

Supporting Videos

Movie S1. CPU spray test by portable spray

References

[1] H. Park, D. Lim, G. Lee, M.-J. Baek, D. W. Lee, *Adv. Funct. Mater.* **2023**, 33, 2305750.

[2] H. M. Yang, I. H. Yoon, Y. Lee, *Chem. Eng. J.* **2020**, 402, 126299.