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Supporting information

Mechanically robust enzymatic degradable shape memory polyurethane urea with rapid recovery response induced by NIR

Xin Li,[a] Wenkai Liu,[a] Yaomin Li,[a] WanLing Lan,[b] Daiguo Zhao,[b] Hecheng Wu,[a] Yuan Feng,[a] Xueling He,[c] Zhen Li,[a] Jiehua Li,*[a] Feng Luo,*[a] and Hong Tan[a]

[a] College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, China;

[b] Sichuan Institute for Food and Drug Control, Chengdu 611731, China;

[c] Laboratory Animal Center of Sichuan University, Chengdu 610041, China.

* Corresponding authors. E-mail: jiehua_li@scu.edu.cn (J.H.L), fengluo@scu.edu.cn (F.L).

Experimental Details

Chemicals

Hexadecyltrimethylammonium bromide (CTAB, > 98.0%), silver nitrate ($AgNO_3$, > 99%), sodium borohydride ($NaBH_4$, 99%), hydrochloric acid (HCl, 37 wt. % in water) were procured from Kelong, Chengdu, China. Tetrachloroauric (III) acid trihydrate ($HAuCl_4 \cdot 3H_2O$), sodium oleate (NaOL, > 99.0%) and L-ascorbic acid (> 99.0%) were supplied from Adamas, Shanghai, China. 2,2'-Dithiodiethanol and 1,4-dithiothreitol (DTT) were purchased from Sigma-Aldrich, USA. Deionized water and ultrapure water used in experiments were obtained from a ULUPURE system.

Synthesis of gold nanorods (GNRs)

According to an established seeded-growth method,[1] the gold nanorods (GNRs) with an aspect ratio of 4 and the longitudinal surface plasmon resonance (LSPR) wavelengths in NIR region were successfully prepared in our laboratory.

To prepare the seed solution, 0.3645 g of CTAB was dissolved in 10 mL of deionized water, followed by addition of 103 μL of $HAuCl_4$ solution (1 mM). Then 0.6 mL of freshly prepared, ice-cold $NaBH_4$ aqueous solution (0.38 mg mL^{-1}) was added into the reaction system. After 2 min vigorous stirring at 1000 rpm, the seed solution was aged at room temperature for 30 min.

The growth solution was prepared as follows: 7.0 g of CTAB and 1.234 g of NaOL were dissolved in 250 mL of warm water (~50 °C) in a 1L round-bottomed flask. Then the solution was cooled down to 30 °C and $AgNO_3$ solution (18 mL, 4 mM) was added. The mixture was kept undisturbed at 30 °C for 15 min after which 250 mL of 1 mM $HAuCl_4$ solution was added. The solution stirred at 700 rpm and became colorless after 90 min. Then 1.5 mL of HCl solution (12.1 M) was introduced to adjust the pH of mixture. After of slow stirring at 400 rpm for another 15 min, 1.25 mL of 0.064 M ascorbic acid (AA) was added and the solution was vigorously stirred for 30 s.

Finally, 0.4 mL of seed solution was injected into the growth solution. The resultant mixture was stirred for 30 s and left undisturbed at 30 °C for 12 h for growth.

Synthesis of PCL-SS-PCL and PCL-SH

Poly(*ε*-caprolactone) disulfide (PCL-SS-PCL), a narrow-distributed polycaprolactone containing a disulfide bond in the middle of the molecule, was synthesized by using the 2,2'-dithiodiethanol as an initiator and tin (II) 2-ethylhexanoate as catalyst according to the method reported by Zhang.[2] The *ε*-caprolactone was used after prior distillation under reduced pressure and the 2,2'-dithiodiethanol was placed in a vacuum oven for 12 h at 50 °C to remove moisture. Typically, *ε*-caprolactone (34.2 g, 0.3 mol) and 2,2'-dithiodiethanol (1.54 g, 0.01 mol) were added into a Shrek bottle and dehydrated at 60 °C for 40 min, followed by adding 122 mg of tin(II) 2-ethylhexanoate into the mixture and the mixture was stirred under vacuum at 120 °C for 12 h. Then the mixture was dissolved in chloroform and precipitated in excess ice methanol. Finally, the precipitate was dried in a vacuum oven at room temperature for 3 days.

PCL-SH can be obtained by reducing the disulfide bond in PCL-SS-PCL. 5.0 g of PCL-SS-PCL and 2.5 g of DTT were dissolved in 50 mL of tetrahydrofuran (THF) and passed nitrogen for 15 min to ensure the reduction reaction was carried out in a nitrogen atmosphere. The mixture

was stirred at room temperature for 12 h. After the reaction completed, the reaction solution was precipitated in excess cold methanol, filtered, and dried in vacuum oven to get the product.

Preparation of PCL-modified gold nanorods (GNRs-PCL)

To achieve a good compatibility between polyurethane and gold nanorods, PCL-SH was tethered onto CTAB-stabilized GNRs *via* ligand exchange.[3] In order to ensure complete reaction, the ratio of CTAB-stabilized GNRs to PCL-SH was set to 1 to 50. Typically, the gold nanorods collected by centrifugation were added dropwise to the PCL-SH/THF solution. The mixture was stirred at room temperature for 24 h. Finally, the PCL-SH-stabilized GNRs (GNRs-PCL) were collected by centrifugation and finally could readily be dispersed in organic phase.

^{1}H-NMR analysis of all PU samples

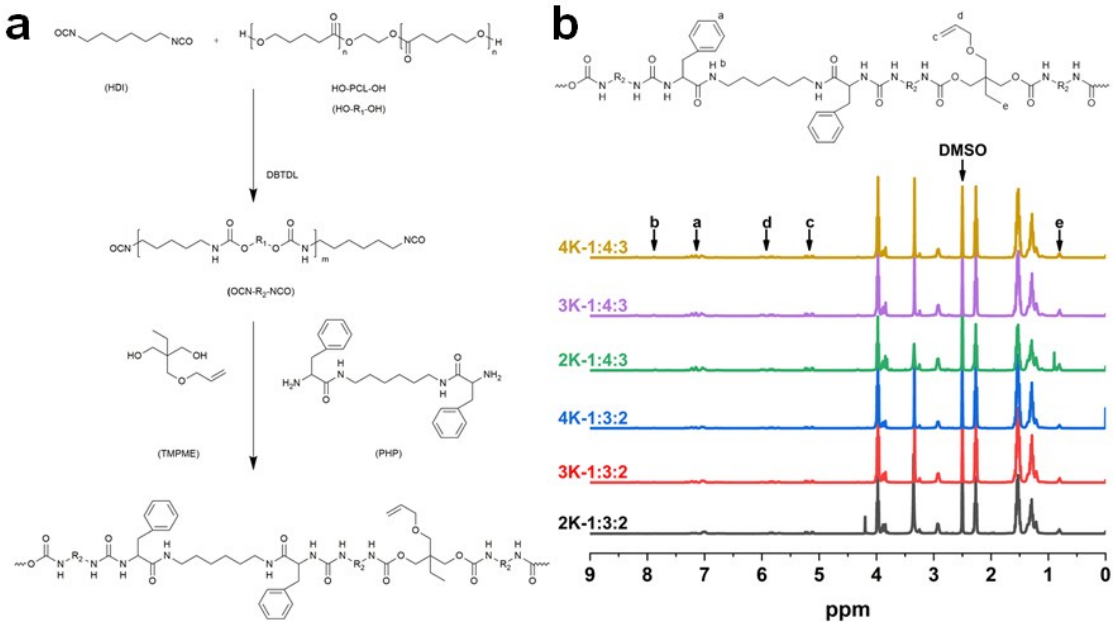

Fig. S1 (a) Schematic diagram of the synthesis of PUs; (b) ^{1}H-NMR spectra of all

polyurethane samples.

Shape memory effect of the series of 1:3:2 samples

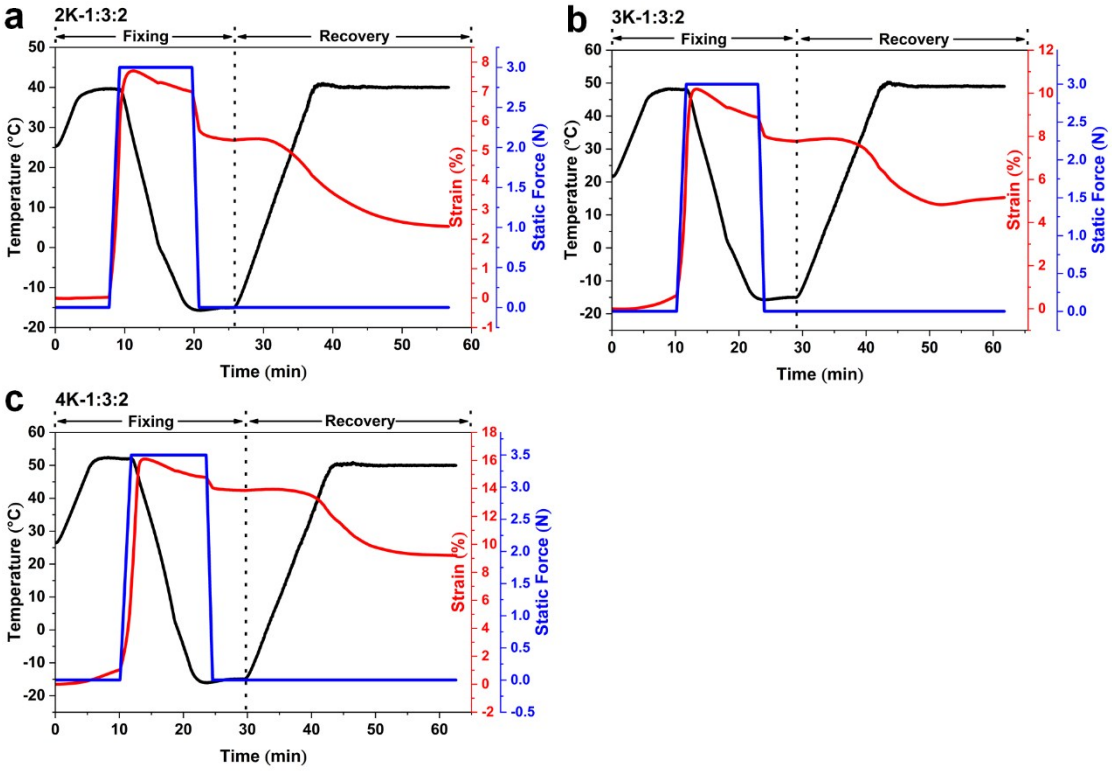

Fig. S2 (a), (b) and (c) The representative diagram of SME for the series of 1:3:2 samples tested by DMA under controlled force mode;

Dynamic thermomechanical analysis of all PU samples

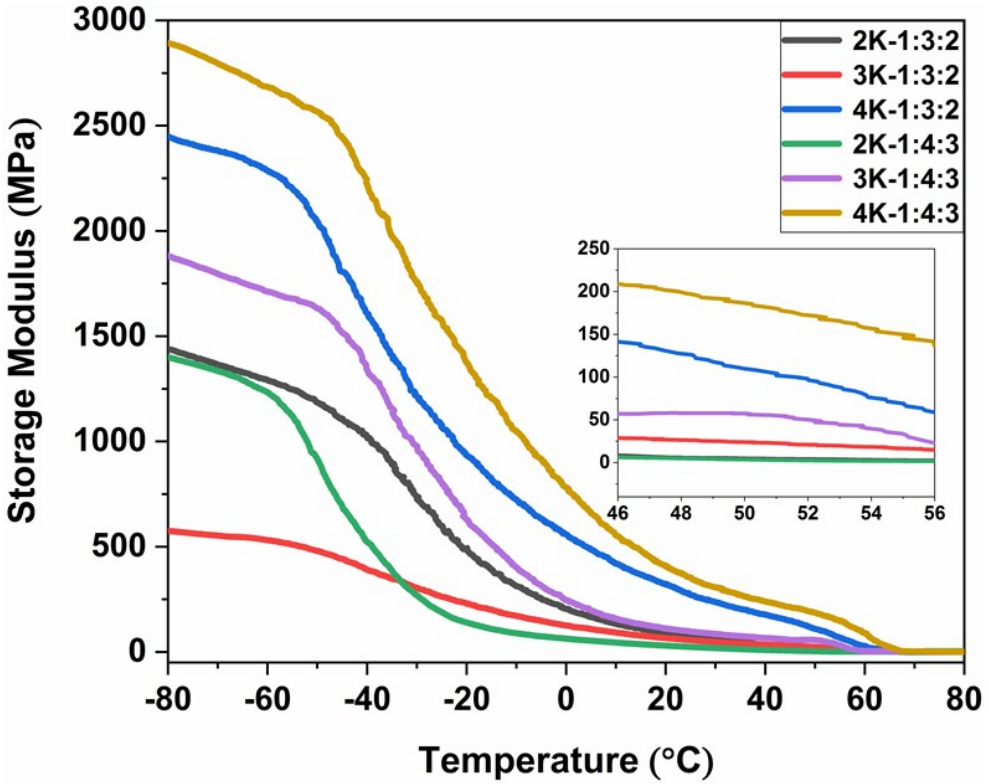

Fig. S3 Dynamic mechanical properties of all polyurethane samples.

Characterization of PCL-SS-PCL and PCL-SH

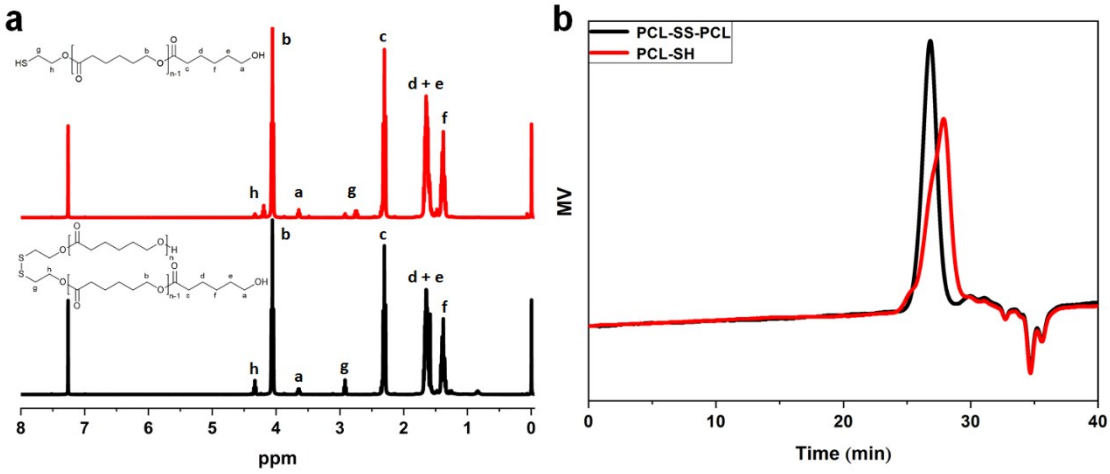

Fig. S4 (a) ^{1}H-NMR spectra of PCL-SS-PCL and PCL-SH in $CDCL_3$; (b) GPC trace of PCL-SS-PCL and PCL-SH.

Table S1 The molecular weight tested of PCL-SS-PCL and PCL-SH by GPC and NMR.

Samples	$\overline{M}_n$[a] (GPC)	$\overline{M}_w$[a] (GPC)	PDI	$\overline{M}_n$[b] (NMR)
PCL-SS-PCL	6352	6837	1.07	3502

PCL-SH	3379	5191	1.53	1881

[a] M_n and M_w were determined by GPC with polystyrene as standards in THF.

[b] M_n was calculated by NMR in $CDCL_3$ at 25 °C.

FTIR analysis of 3K-1:4:3 composites and 4K-1:4:3 composites

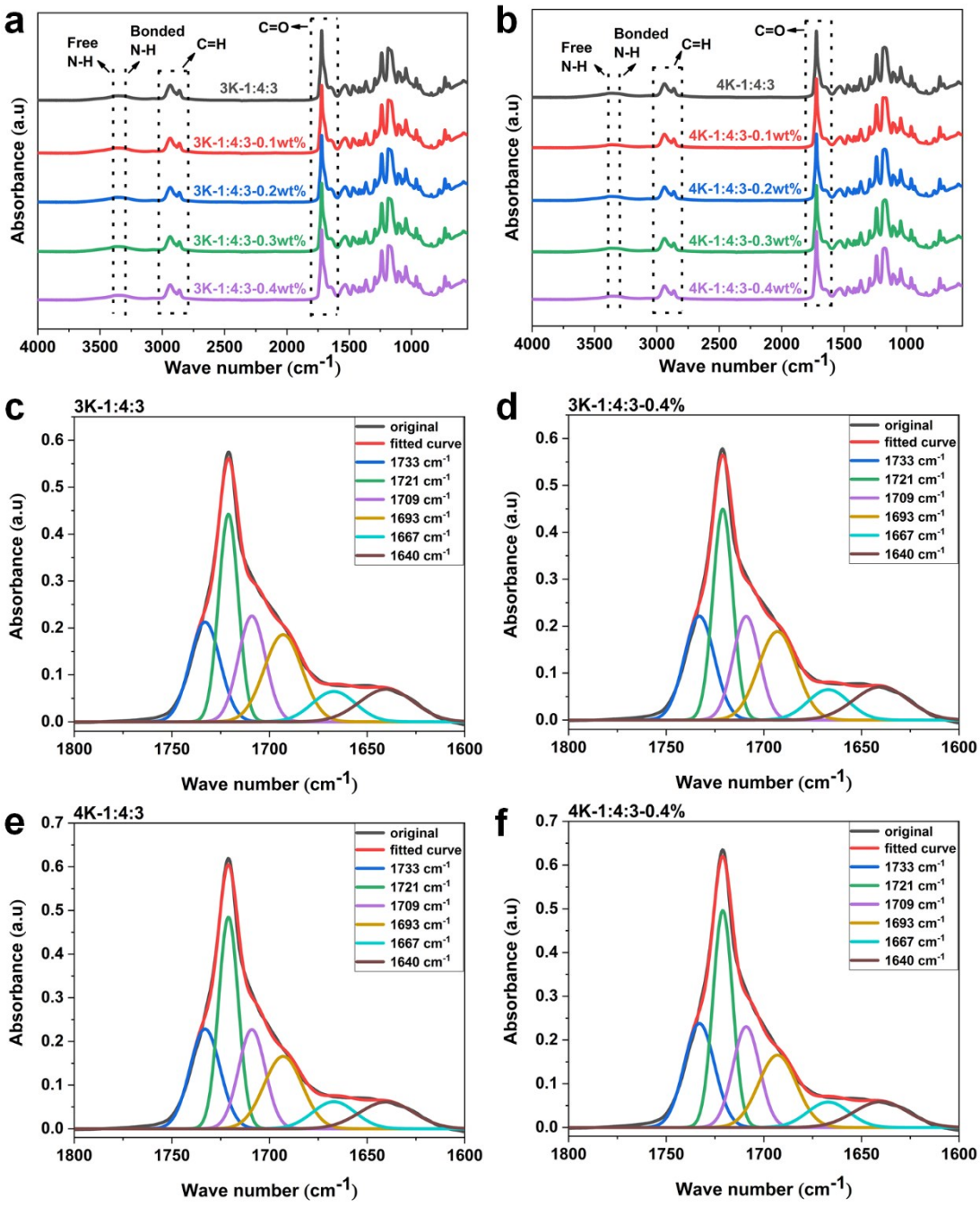

Fig. S5 (a) Full FTIR spectra of 3K-1:4:3 composites from 400 to 4000 cm^{-1}; (b) Full FTIR spectra of 4K-1:4:3 composites from 400 to 4000 cm^{-1}; (c) and (d) Fitting

curves for 3K-1:4:3 and 3K-1:4:3-0.4wt%, respectively; (e) and (f) Fitting curves for 4K-1:4:3 and 4K-1:4:3-0.4wt%, respectively.

Table S2 Assignment of the Absorption Bands in the Carbonyl Region of the FTIR Spectra for PUUs.

Wave number (cm^{-1}) of peaks	Assignments
1733	Free carbonyl stretching of PCL
1721	Hydrogen-bonded carbonyl of PCL
1709	Free carbonyl stretching for urethane linkages
1693	Hydrogen-bonded carbonyl for urethane linkages
1667	Free carbonyl stretching for urea linkages
1640	Hydrogen-bonded carbonyl for urea linkages

Table S3 FTIR curve-fitting results of 3K-1:4:3; 3K-1:4:3-0.4wt%; 4K-1:4:3 and 4K-1:4:3-0.4wt% in carbonyl stretching region.

Samples	Peak area (%)						Proportion of 1733 cm^{-1}
	1733 cm^{-1}	1721 cm^{-1}	1709 cm^{-1}	1693 cm^{-1}	1667 cm^{-1}	1640 cm^{-1}	
3K-1:4:3	18.5	25.0	17.6	20.2	8.0	10.8	18.5%
3K-1:4:3-0.4wt%	19.1	25.4	16.6	20.4	7.5	11.0	19.1%
4K-1:4:3	19.8	27.5	17.4	18.2	7.6	9.5	19.8%
4K-1:4:3-0.4wt%	20.7	28.0	17.5	18.0	6.9	9.1	20.7%

Enzymatic degradability experiment.

The PU films were placed in the chymotrypsin/PBS solution, and incubated in a shaker at 37 °C. Based on the literature[4] and previous work,[5] the concentration of chymotrypsin/PBS solution was set to 0.3 g L^{-1}. The degradation solution was replaced every two days. The degradation process was assessed by mass loss and scanning electronic microscopy (SEM). The corroded surfaces were observed by SEM (Nova

Nano SEM450, FEI, USA) at days 1, 3, 6, 10, 15, 20, 25 and 30. Also, the samples were dried and weighed at days 1, 3, 6, 10, 15, 20, 25 and 30, respectively. Samples mass as a percentage of initial mass is calculated as follows:

$$\text{Residual weight } (\%) = \frac{\text{Final Film Segment Mass}}{\text{Initial Film Segment Mass}} \times 100\% \qquad (1)$$

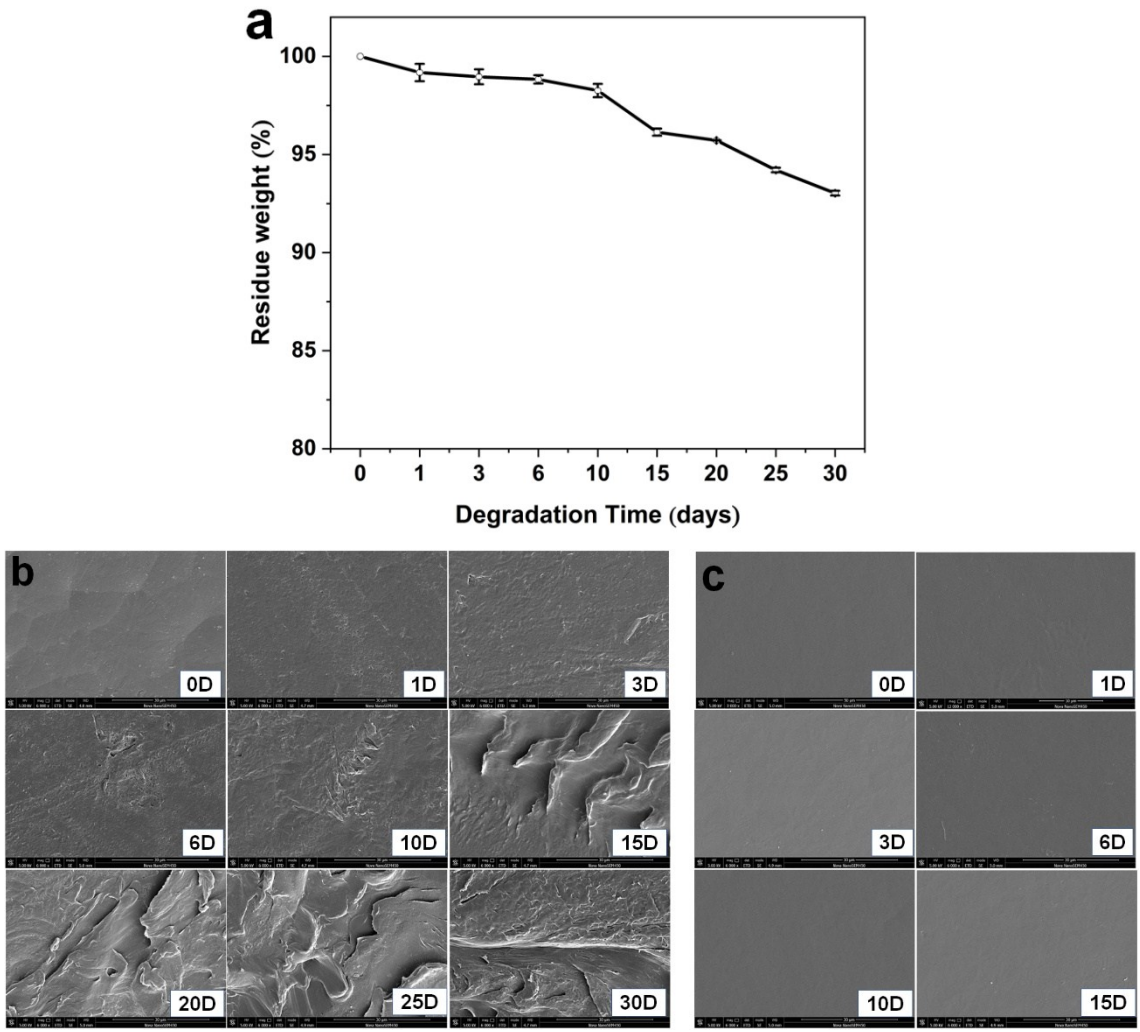

Fig. S6 (a) Residual weight as a function of time during degradation of 4K-1:4:3; (b) SEM micrographs of the 4K-1:4:3 after 0, 1, 3, 6, 10, 15, 20, 25 and 30 days of chymotrypsin/PBS degradation; (c) SEM micrographs of the control sample without PHP after 0, 1, 3, 6, 10 and 15 days of chymotrypsin/PBS incubation.

References

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