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Improved in Vivo Stability of Silicon-containing Polyurethane by Fluorocarbon Side Chain Modulating the Surface Sructure

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Supplementary Information

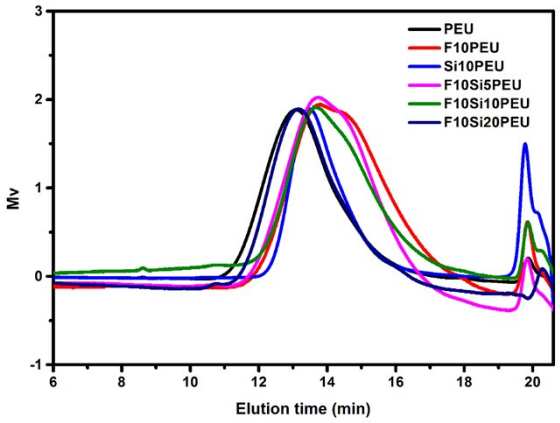

Fig. S1 GPC traces for original samples. The molecular weight distribution is relatively uniform.

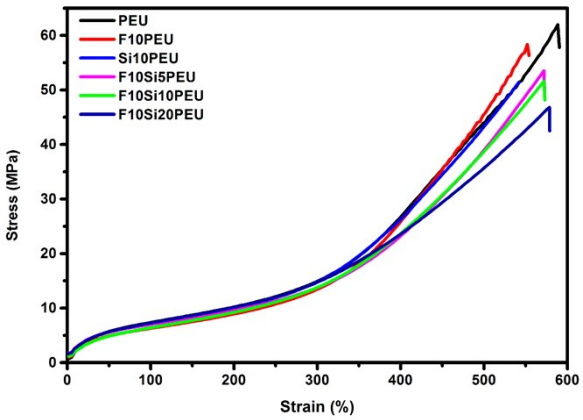

Fig. S2 Stress-strain curves of PEUs. PEU has the best breaking elongation and breaking strength. As the silicon content increases, the mechanical properties decrease. But they are maintained at a good mechanical performance.

Table S1. The fractions of three carbonyls from transmission FTIR by curve fitting.

Sample	1700 cm^{-1} (%) [a]	1715 cm^{-1} (%) [b]	1735 cm^{-1} (%) [c]
PEU	52.34	14.83	32.83
F10PEU	42.06	12.43	45.51
Si10PEU	56.89	10.87	32.24
F10Si5PEU	53.69	12.65	33.66
F10Si10PEU	49.99	12.53	37.48
F10Si20PEU	55.44	11.93	32.63

[a] strongly hydrogen-bonded carbonyls. [b] loosely hydrogen-bonded carbonyls. [c] free (non-bonded) carbonyls.

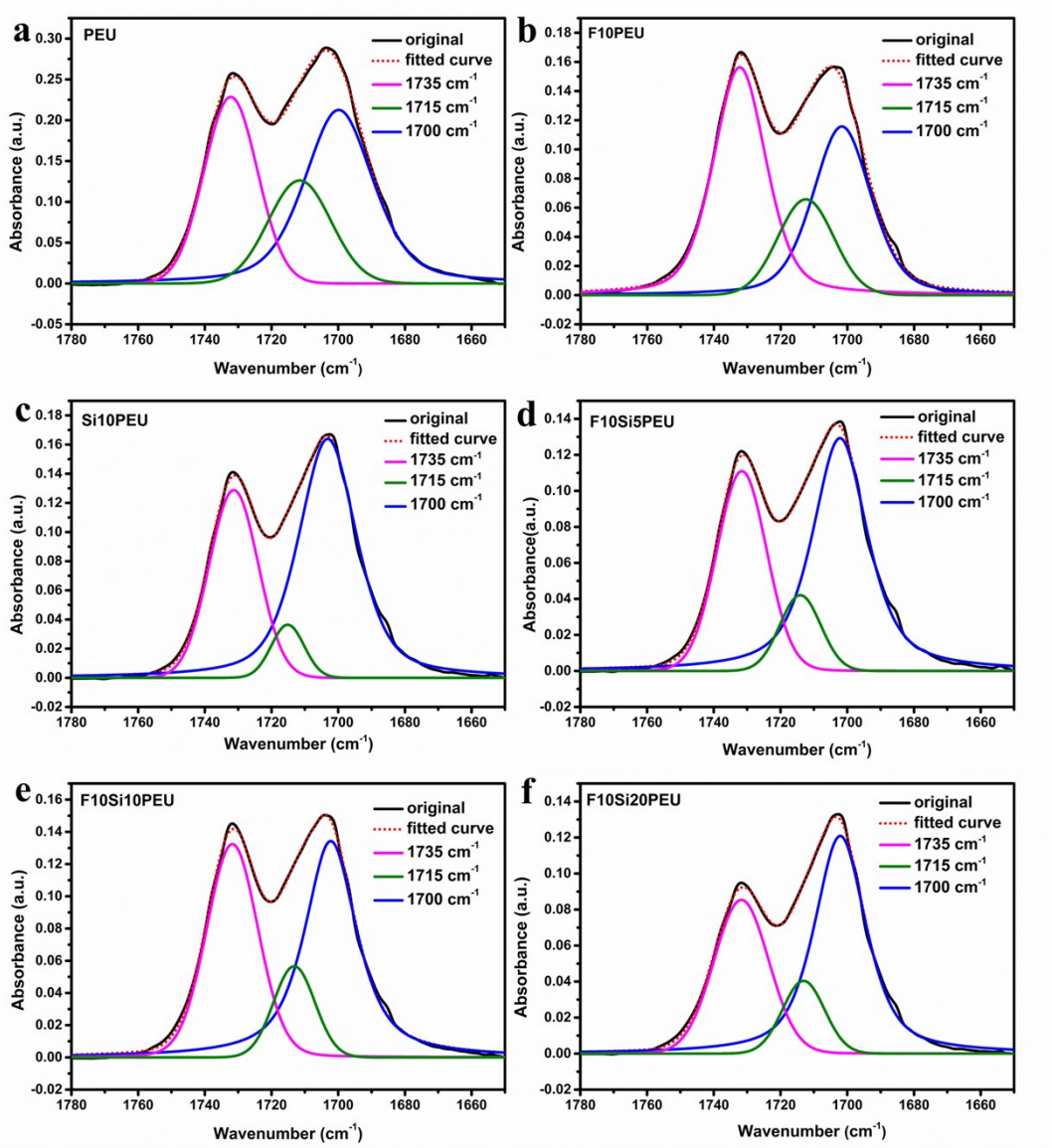

Fig. S3 The fitting curve results of carbonyl transmission FTIR from 1650 to 1800 cm^{-1}. The proportion of strongly hydrogen-bonded carbonyls of SiPEUs significantly larger than that of other groups. And F10PEU is the least. Free (non-bonded) carbonyls are just the opposite.

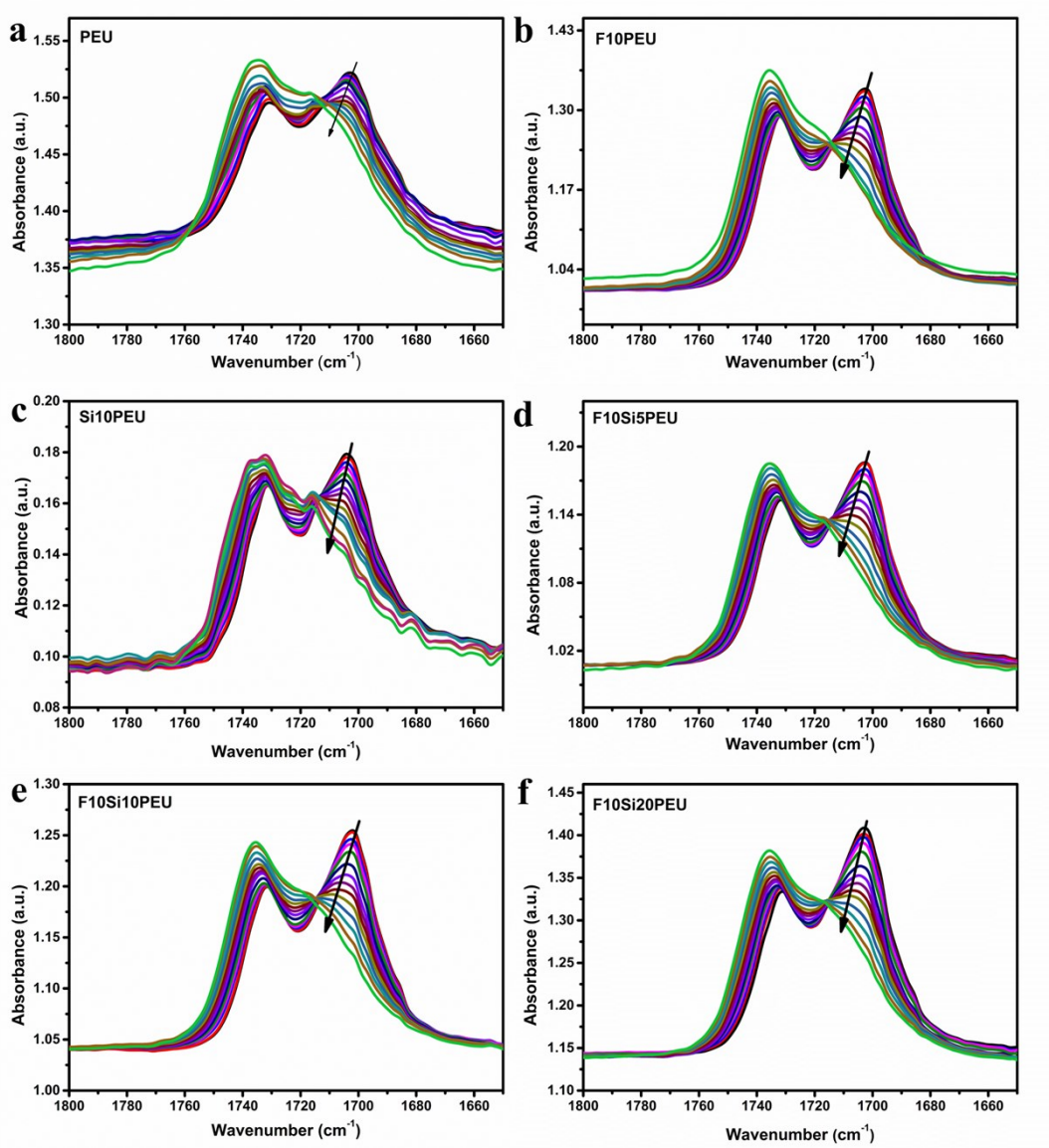

Fig. S4 Temperature-controlled transmission FTIR spectra of PEUs. As temperature increased, the strongly hydrogen-bonded carbonyls of PEUs at 1700 cm^{-1} gradually decreased and moved toward a high wave number. The free carbonyl peaks of PEUs at 1735 cm^{-1} increased and moved to higher wavenumbers. And the bands widen.

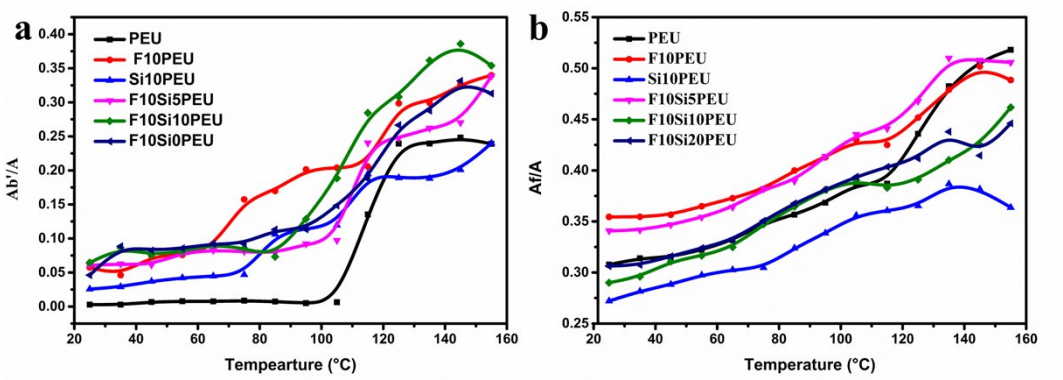

Fig. S5 Statistics of carbonyl curve fitting results of FTIR spectra at different temperatures. (a) and (b) The relative fractions of loosely hydrogen-bonded carbonyls and the relative fractions of free (non-bonded) carbonyls.

Table S2. Transition temperatures and enthalpies of PEUs from DSC.

Smple	Soft segment		C_pSP	T_{m1}	T_{m2}	T_c	H_{m1}	H_{m2}	H_c
	T_{g1}	T_{g2}							
PEU	-	-45.54	0.49	62.64	109.15	49.88	5.43	5.43	1.95
F10PEU	-	-43.81	0.49	60.67	108.85	-	5.05	5.05	-
Si10PEU	-128.09	-43.87	0.43	59.08	107.46	50.31	2.4	2.4	2.02
F10Si5PEU	-	-42.41	0.49	62.00	108.60	-	3.72	3.72	-
F10Si10PEU	-128.28	-40.30	0.42	62.93	108.88	-	4.23	4.23	-
F10Si20PEU	-126.65	-41.67	0.35	62.54	110.10	53.41	3.49	3.30	5.80

Table S3. Transition temperatures and loss factor from DMA.

Sample	T_{g1}	Tan δ_1	T_{g2}	Tan δ_2	E' (MPa) T_g+50
PEU	-	-	-22.56	0.43	26.62
F10PEU	-	-	-21.69	0.55	19.90
Si10PEU	-123.22	0.093	-17.72	0.46	19.75
F10Si5PEU	-124.20	0.078	-19.43	0.45	18.12
F10Si10PEU	-124.07	0.093	-15.74	0.50	12.54
F10Si20PEU	-122.77	0.115	-15.67	0.41	16.35

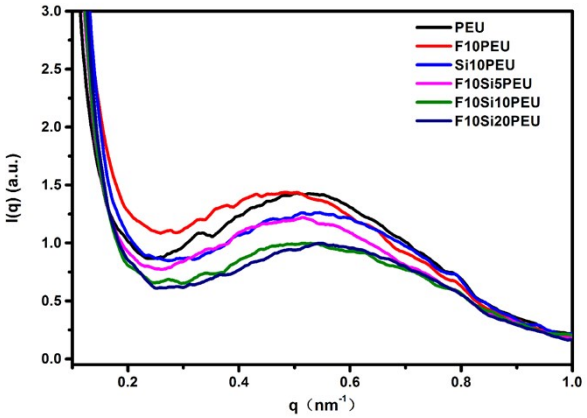

Fig. S6 Curves of synchrotron SAXS scattering patterns for PEUs. The introduction of FDO reduced the value of q_{max}. The introduction of PDMS increases the q_{max} value.

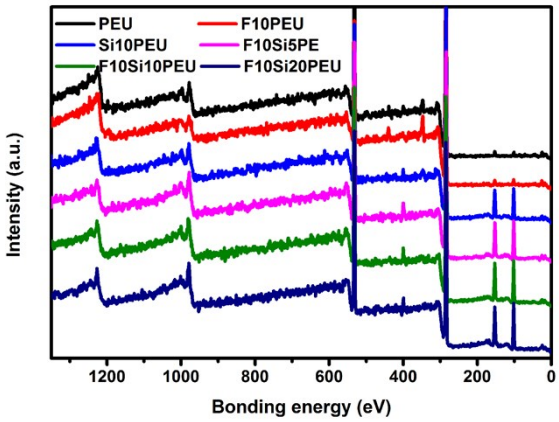

Fig. S7 XPS spectra of PEUs. The silicon content of F10Si5PEU is higher than that of Si10PEU.

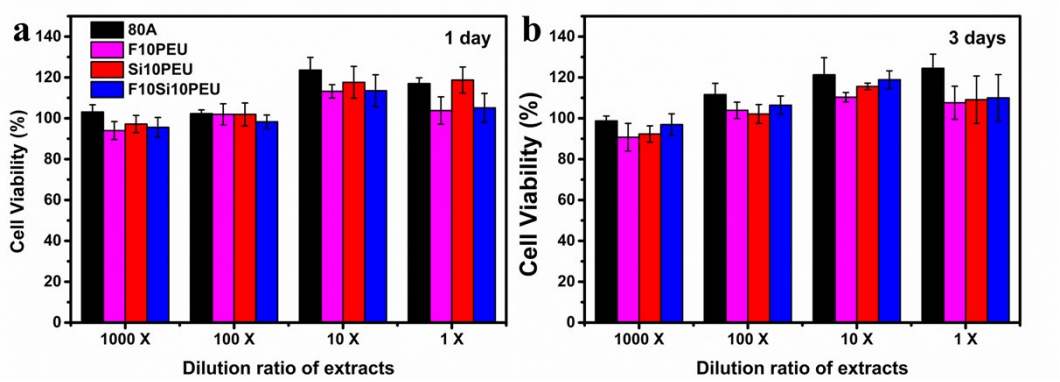

Fig. S8 Cytotoxicity of cultured L929 cells after dilution with PEUs extract for 1 day (a) and 3 days (b) (n=3). The dilution factor is 1×, 10 ×, 100 × and 1000 ×. Negative control is pure medium. All materials show good cell viability (>90%).

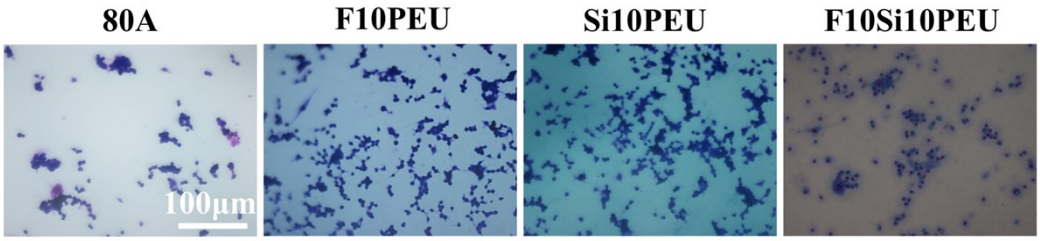

Fig. S9 The morphology and number of macrophages cultured for 7 days in vitro on the surface of the materials.

Table S4. Summary of apoptosis data of macrophages in vitro culture.

Time	Sample	Necrotic cells (UL) (%)	Necrotic or late apoptotic cells (UR) (%)	Viable cells (LL) (%)	Early stage apoptotic cells (LR) (%)	Total apoptotic cells
24h	80A	1.04	7.30	80.57	11.10	18.39
	F10PEU	1.22	7.50	83.76	7.49	15.02
	Si10PEU	2.00	6.20	86.47	5.29	11.53
	F10Si10PEU	1.46	6.00	85.18	7.33	13.36
48 h	80A	1.54	9.80	80.11	8.55	18.35
	F10PEU	3.38	32.00	58.18	6.86	38.44
	Si10PEU	1.39	21.00	68.30	8.84	30.31
	F10Si10PEU	4.31	39.00	50.63	6.00	45.06

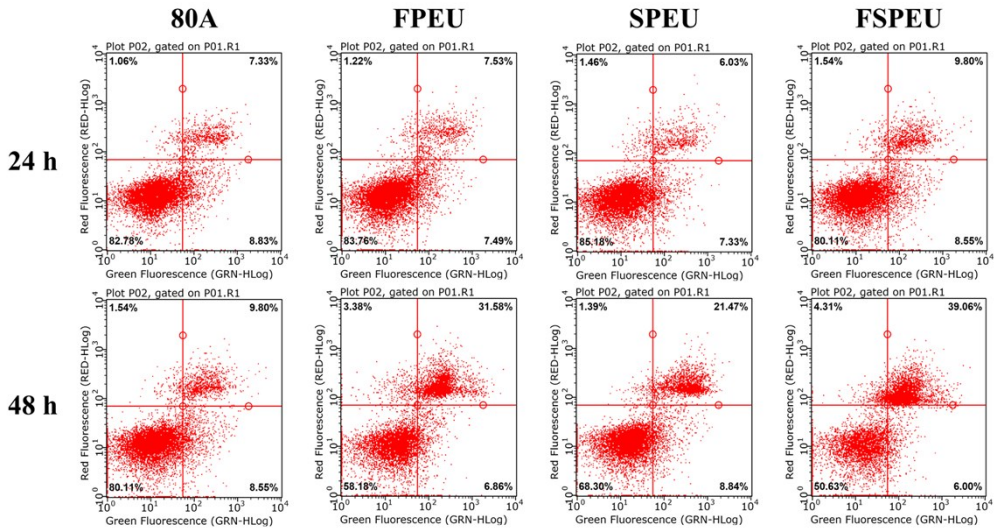

Fig. S10 Apoptosis by flow cytometry.

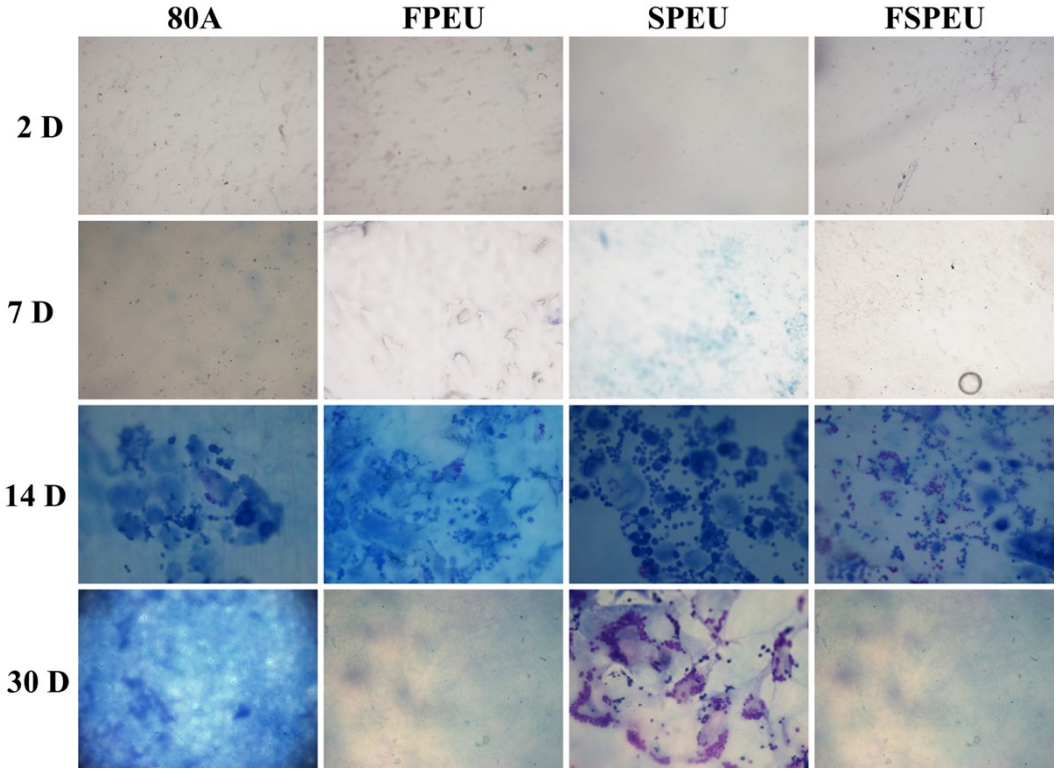

Fig. S11 Cell state on the surfaces of implanted material in vivo. There are only a few cells on the material surface.

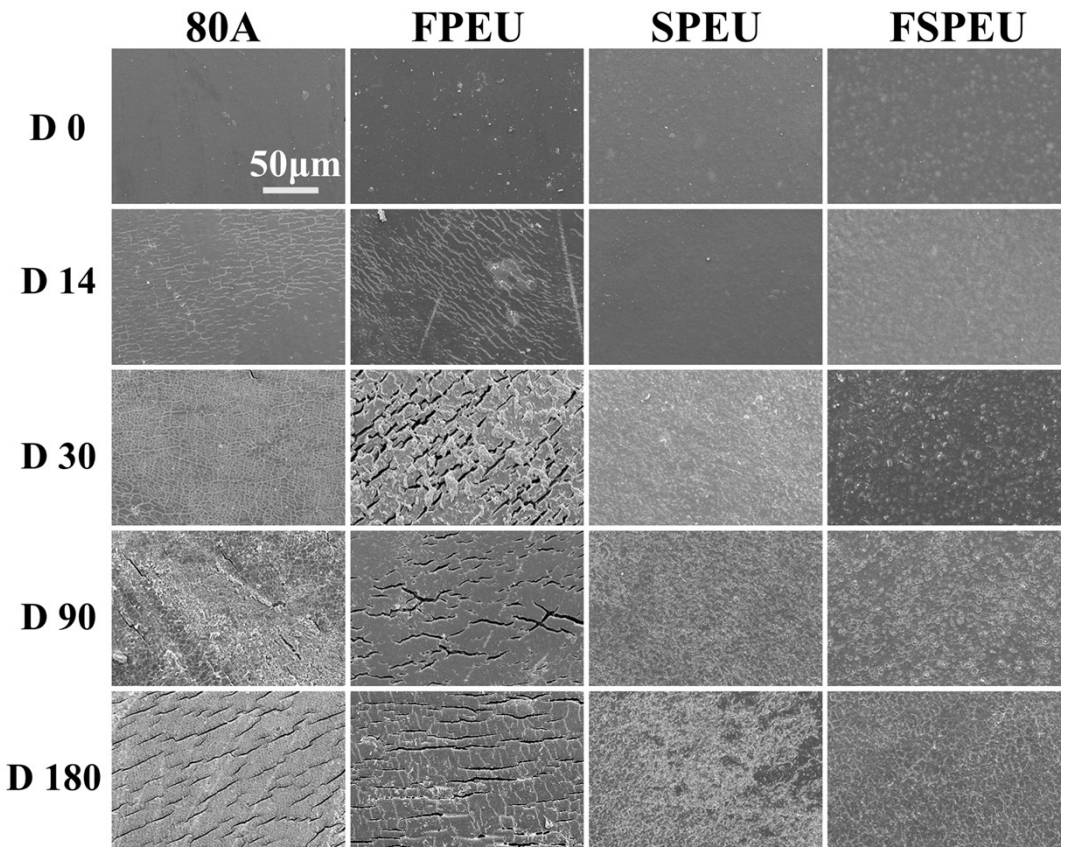

Fig. S12 SEM at different biodegradation times (×2000). After implantation in the body for 14 days, obvious cracks have appeared on the surface of 80A and F10PEU. Under 2000 times, the difference between Si10PEU and F10Si10PEU is not obvious, high multiples can be obtained from Fig. 7.

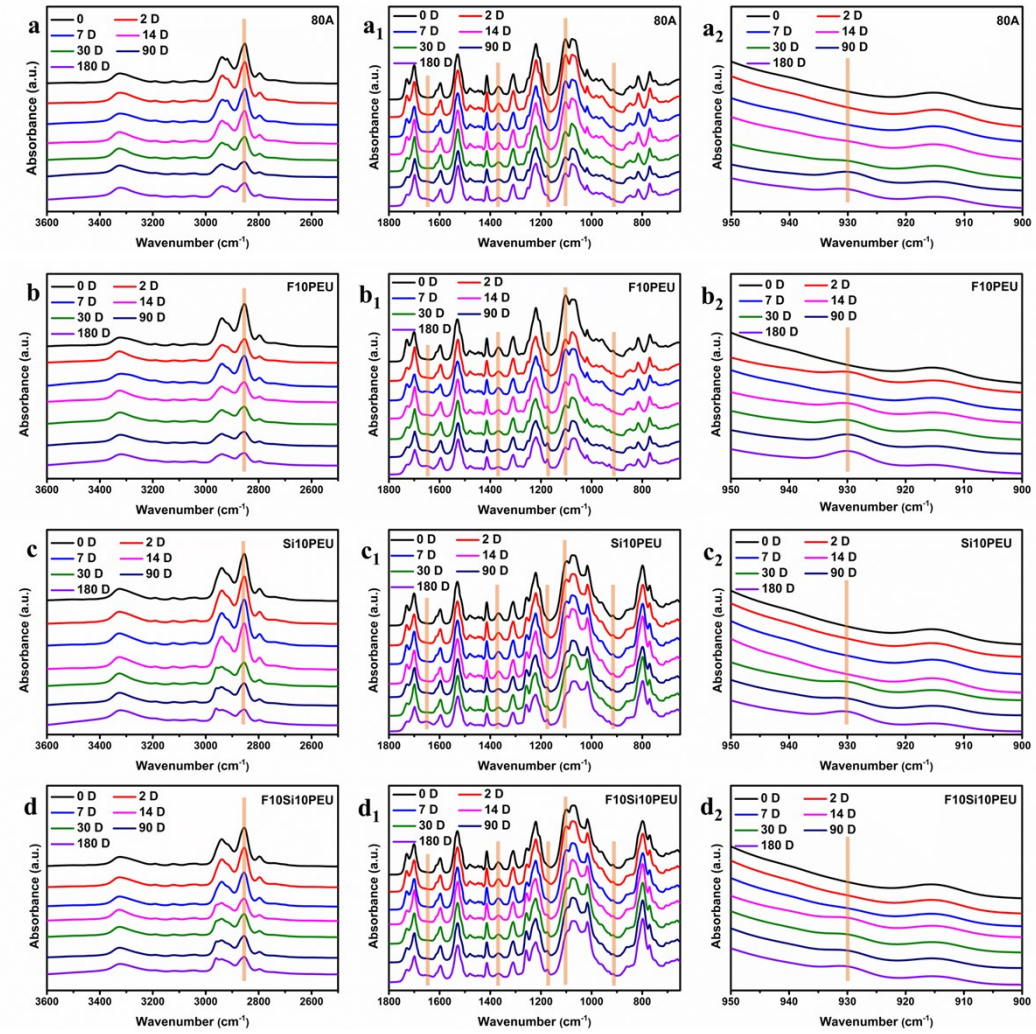

Fig. S13 Infrared spectra of samples at different implantation times by ATR-FTIR.

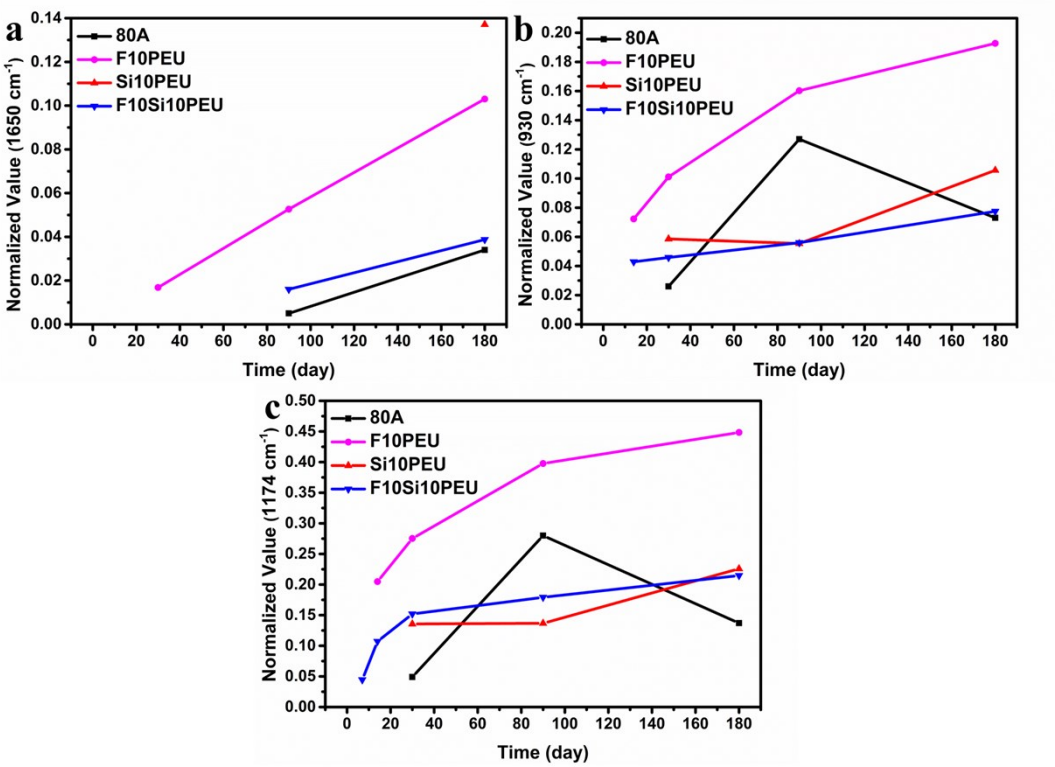

Fig. S14 (a), (b) and (c) The normalized value from infrared spectra at 1650, 1174 and 930 cm^{-1} of the samples implanted at different times, respectively.

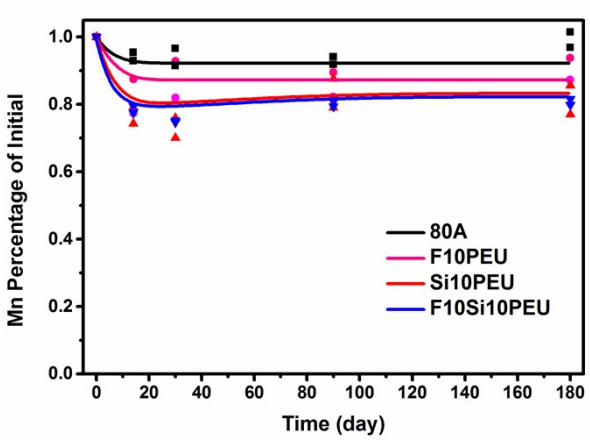

Fig. S15 M_n percentage of initial after implantation for different times.

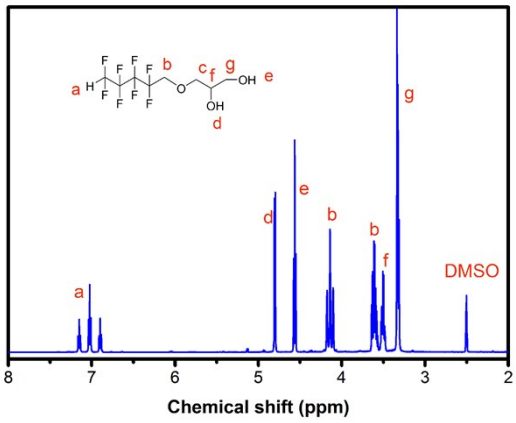

Fig. S16 ^{1}H NMR spectrum of FDO. ^{1}H NMR (DMSO-d6, 400MHz): δ=7.02 (-CF_2H, a), δ=4.8 (-CH-OH, d), δ=4.56 (-CH_2-OH, e), δ=4.12 (-CF_2-CH_2-O-, b), δ=3.61 (-CH_2-O-CH_2-CH-, c), δ=3.50 (-CH2-O-CH2-CH-, f), δ=3.31 (-CH-CH2-OH, g).

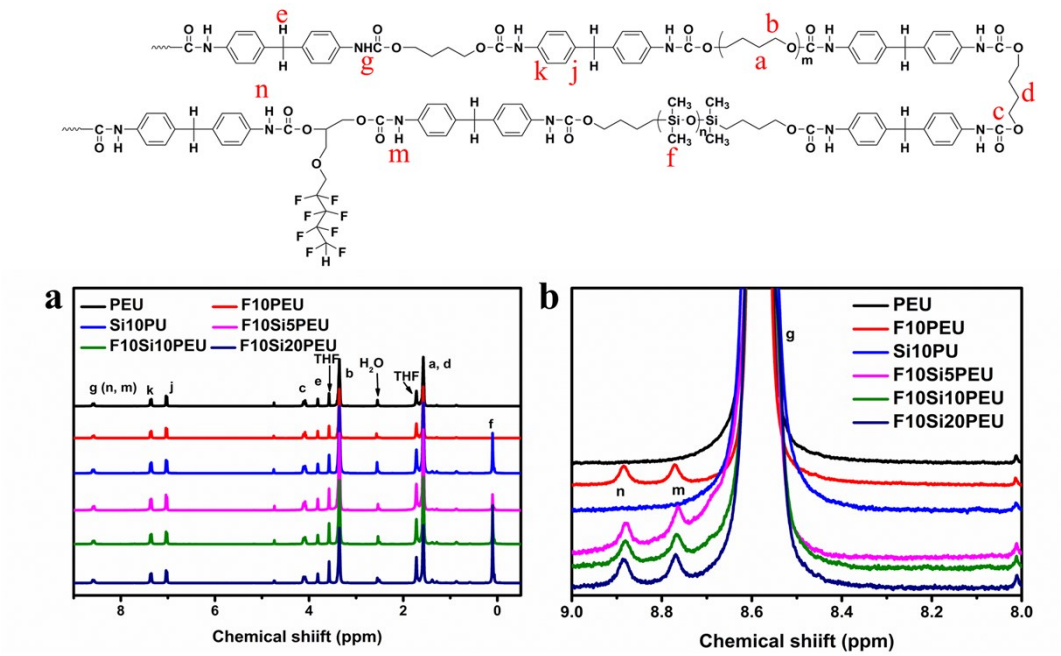

Fig. S17 ^{1}H NMR spectra of PEUs. (a) Full-spectrum ^{1}H NMR of PEUs. The characteristic peaks of PEUs can be found. Silicon-containing polyurethanes has a characteristic peak of Si-CH_3 at about 0 ppm. (b) ^{1}H NMR spectra of PEUs in the range of 8-9 ppm. ^{1}H NMR (THF-d8, 400MHz): δ=8.89 (Ar-N<u>H</u>-(CO)-O-CH-CH_2-O-, n), δ=8.77 (Ar-N<u>H</u>-(CO)-O-CH2-CH-O-, m), δ=8.58 (Ar-N<u>H</u>-(CO)-O-CH_2-CH_2-, g), δ=7.36 (ArH, k), δ=7.02 (ArH, j), δ=4.09 (-NH-(CO)-O-C<u>H</u>$_2$-CH_2-CH_2-CH_2-, c), δ=3.80 (Ar-C<u>H</u>$_2$-Ar, e), δ=3.36 (-O-CH_2-CH_2-CH_2-C<u>H</u>$_2$-O-CH_2-,b), δ=1.61 (-NH-(CO)-O-CH_2-CH_2-C<u>H</u>$_2$-CH_2-O-, d), δ=1.57 (-O-CH_2-CH_2-C<u>H</u>$_2$-CH_2-O-CH_2-, a), δ=0.10 (-Si(C<u>H</u>$_3$)$_2$-O-, f). The N-H in the carbamate formed by the reaction of FDO and isocyanate was found. ^{1}H NMR proved that PDMS and FDO were successfully introduced into polyurethanes.

Aknowledgements

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