Supporting Information

Tyramine functionalization of poly(glycerol sebacate) increases the elasticity of the polymer

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1. Proton NMR analysis to identify the chemical compositions of PGS-SA and PGS-TA

The actual contents of succinate and tyramine in PGS-SA and PGS-TA prepolymers are quantified by proton NMR spectroscopy (**Fig. S1**). The integral area ratio of H_{i+j} to H_d is used to determine the actual succinate in PGS-SA (**Fig S1A**). Similarly, the actual contents of tyramine in PGS-TA$_{15}$ and PGS-TA$_{25}$ are calculated according to the integral area ratio of H_{n+o} to H_d (**Fig. S1B and C**). The detailed calculations are shown in equations (1), (2) and (3).

$$\frac{(2H_i+2H_j)x}{4H_d(x+y)} = \frac{A_{H_i}+A_{H_j}}{A_{H_d}} = \frac{0.8353+0.7993}{12.7511}, x = 13\% \qquad (1)$$

$$\frac{(2H_n+2H_o)x}{4H_d(x+y)} = \frac{A_{H_n}+A_{H_o}}{A_{H_d}} = \frac{0.8921+0.8793}{10.4007}, x = 17\ \% \qquad (2)$$

$$\frac{(2H_n+2H_o)x}{4H_d(x+y)} = \frac{A_{H_n}+A_{H_o}}{A_{H_d}} = \frac{0.8561+0.8622}{6.5003}, x = 26\ \% \qquad (3)$$

Where x + y = 1. The actual succinate content in PGS-SA is determined to be 13 mol%. Compared to the theoretical 25 mol%, approximately 52 % of succinic anhydride was reacted with

PGS to yield the intermediate PGS-SA. However, the actual tyramine contents in PGS-TA_{15} and PGS-TA_{25} are 17 and 26 mol% respectively, which are close to the theoretical values of 15 and 25 mol%. This result indicates that the coupling reaction of tyramine with PGS-SA was occurred nearly in a quantitative fashion. The integration measurements likely introduced some errors, leading to the actual contents slightly higher than the theoretical values.

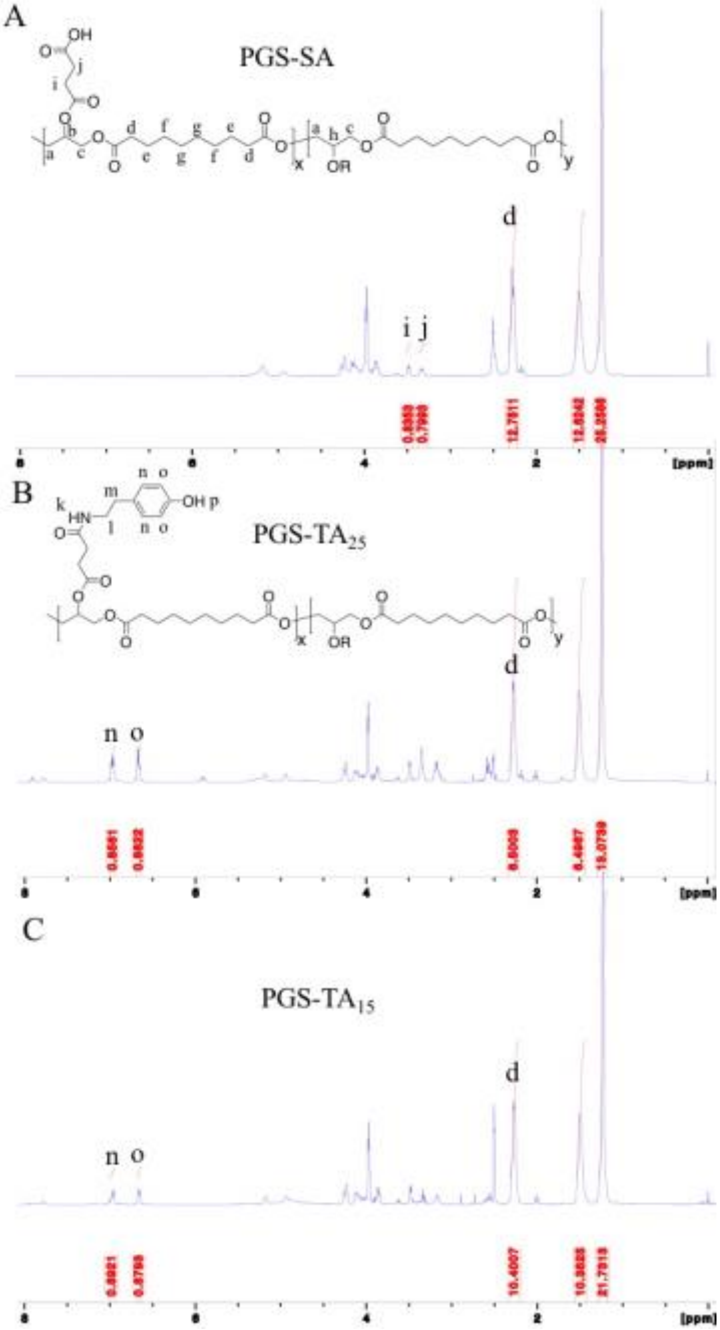

Fig. S1 (A) Integral area ratio of H_{i+j} to H_d is used to determine the actual composition of succinate in PGS-SA. Integral area ratio of H_{n+o} to H_d is used to determine the actual composition of tyramine in (B) PGS-TA_{25} and (C) PGS-TA_{15}.

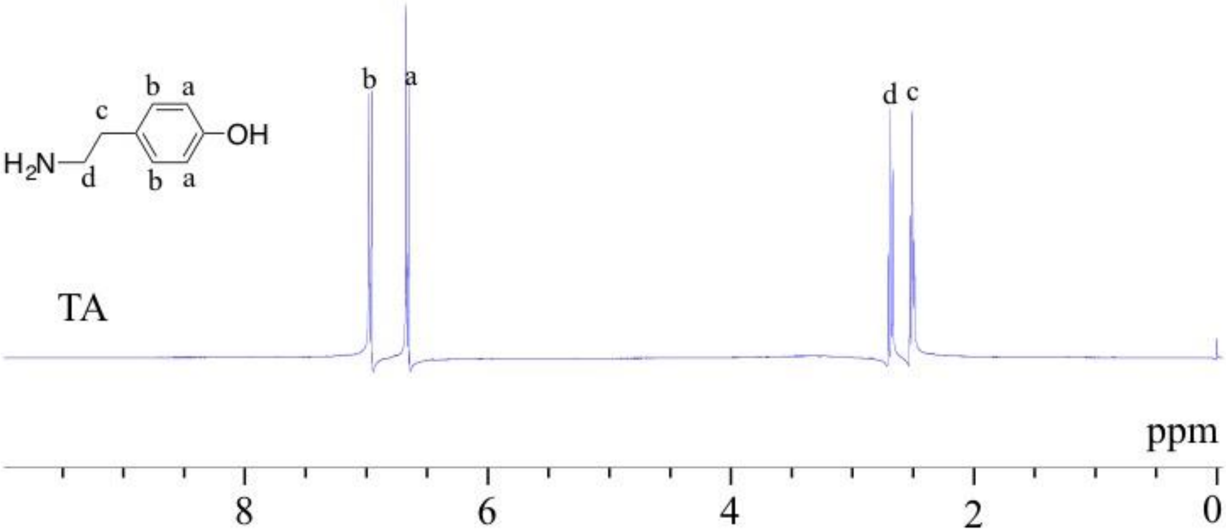

Fig. S2 Proton NMR spectrum of tyramine. The integral area ratio of H_a:H_b:H_c:H_d is approximately 1:1:1:1, matching well with the chemical structure of tyramine.

2. GPC analysis

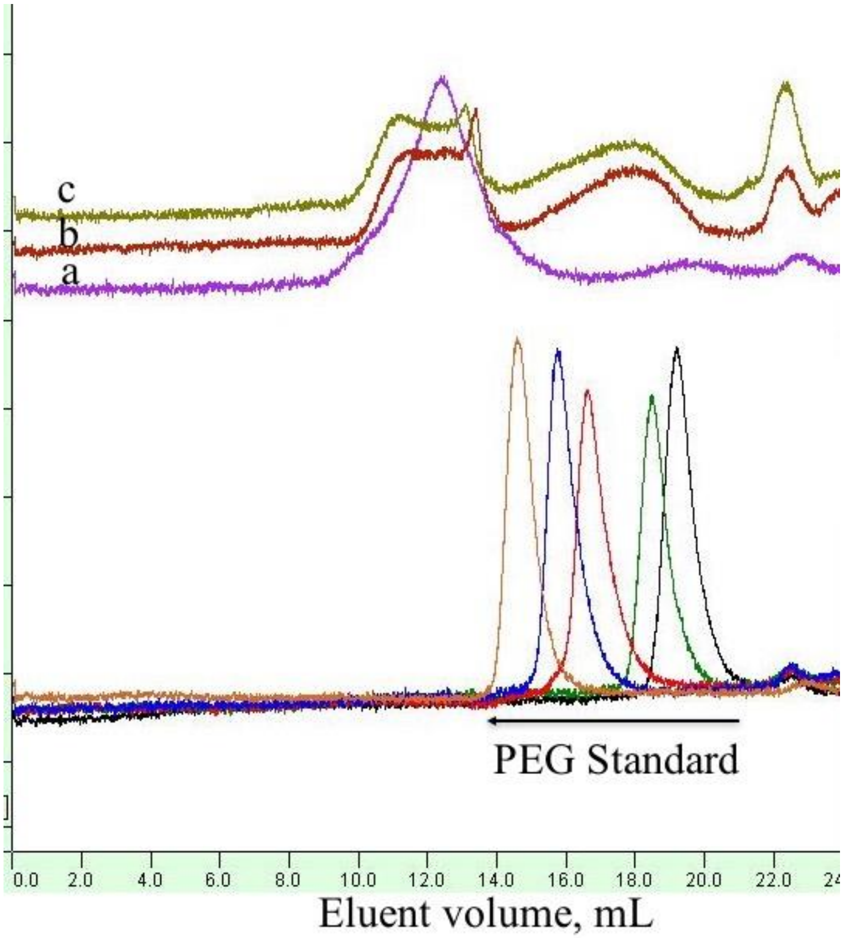

Fig. S3 Comparison of the molecular weight distribution by gel permeation chromatography (GPC) using PEG as standards. (a) PGS-SA, (b) PGS-TA$_{15}$ and (c) PGS-TA$_{25}$. Molecular weight (Mn) of the PEG standards from right to left (arrow direction) are 1840, 2800, 10600, 22100, 106000 Da. After PGS-SA is coupled with tyramine, both PGS-TA$_{15}$ and PGS-TA$_{25}$ show high molecular weight bands above 106000 Da and low molecular weight bands between 1840 to 22100 Da referring to the PEG standards. It appears that tyramine molecules not only reacted with the immobilized succinate in PGS-SA, but some polyesters were also broken down into short chains, likely due to aminolysis of the ester bonds with tyramine.

3. Mechanical properties test

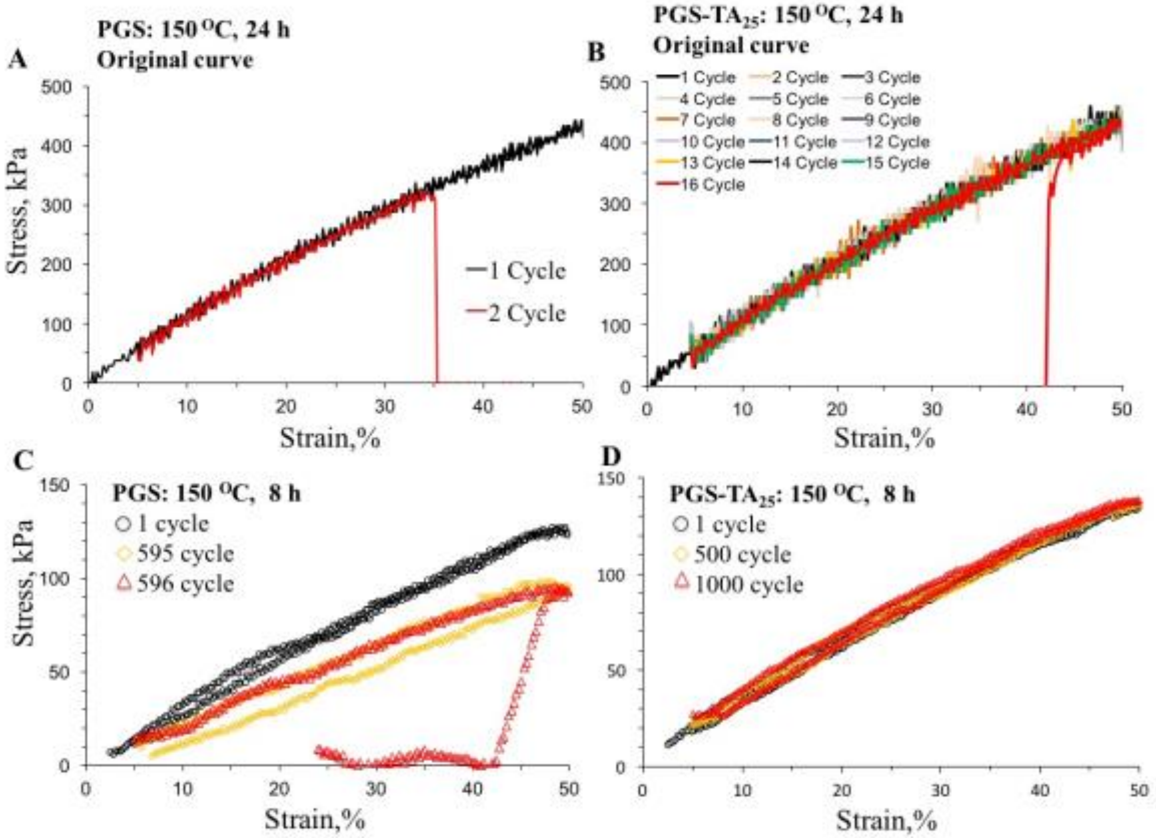

Fig. S4 (A, B) The representative original stress-strain curves from the cyclic loading tests of the PGS control and PGS-TA$_{25}$ elastomers. Both elastomers were made by curing at 150 °C for 24 h. (C, D) Cyclic loading tests of the PGS control and PGS-TA$_{25}$ elastomers that were cured at 150 °C for 8 h. Reduction of curing time increased the cyclic loading number from 1 to 595 cycles for the PGS control and 16 to more than 1000 cycles for PGS-TA$_{25}$ elastomers (We stopped the cyclic loading test at 1000 cycles without breaking the sample.). The tyramine functionalities significantly enhanced the capability to tolerate elastic deformations compared to PGS alone.

Please note that here we demonstrated one representative of the original stress-strain curve for each sample. We replicated at least three times for the cyclic loading tests for each PGS control, PGS-TA$_{15}$ and PGS-TA$_{25}$ elastomer, respectively. The average cyclic numbers are obtained to present in the main text in **Fig. 4A**. Because our mechanical test instrumentation (MTS Insight^{TM} instrument, MTS Systems Corp., MN, USA) is not suitable for testing this type of soft elastomer, so the original curves are fluctuating (**Fig. S4A, B**). Therefore, we processed the original data by averaging 21 data points to obtain the relatively smooth curves for use.

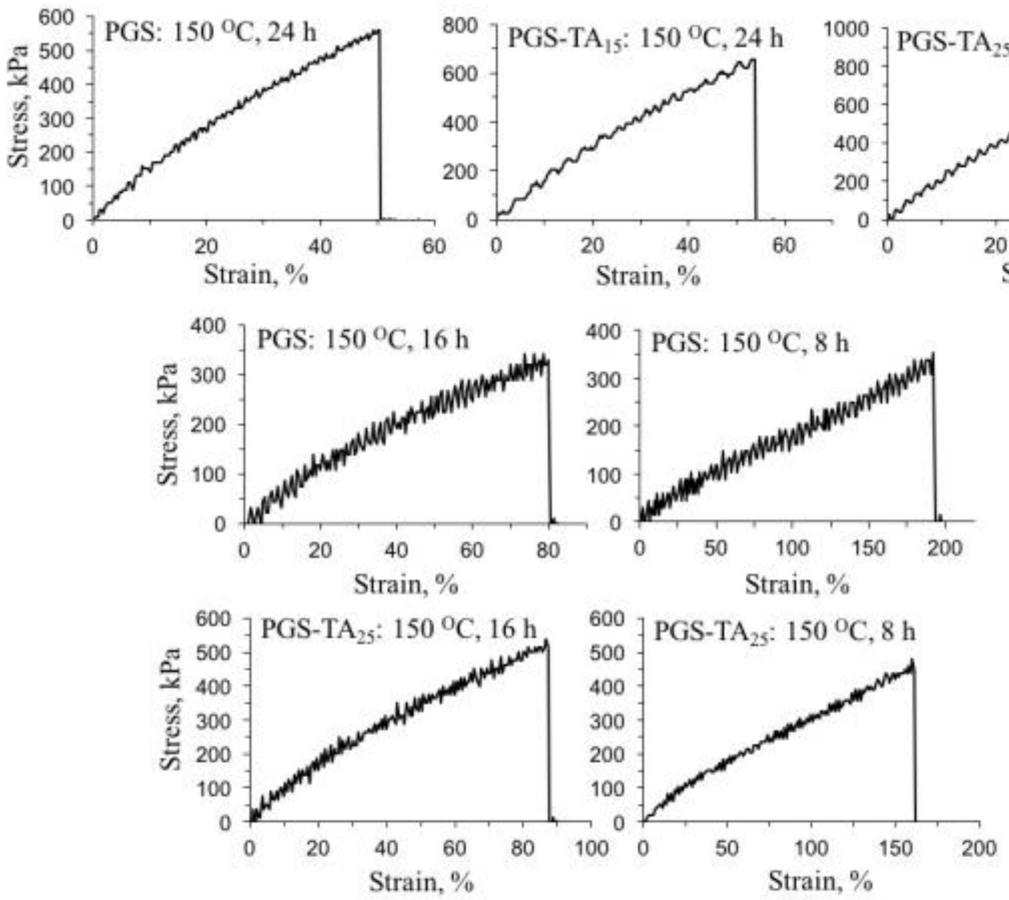

Fig. S5 Examples of the original stress-strain curves from tensile tests of PGS control, PGS-TA$_{15}$ and PGS-TA$_{25}$ elastomers. Each sample was replicated more than 4 times for tensile tests and one representative stress-strain curve for each sample is shown here.

The original data points are fluctuating using our MTS instrument, so each stress-strain curve was processed by averaging 13 data points to obtain a relatively smooth curve to work out strain at fracture, ultimate tensile strength (UTS) and Young's modulus (E). We could not merge all replicates of the stress-strain curves in one figure using microsoft excel, so we list the strain at fracture, UTS and E from each stress-strain curve in **Table S1** for reference.

Table S1 Strain at fracture, ultimate tensile strength (UTS) and Young’s modulus (E) of the PGS control, PGS-TA$_{15}$ and PGS-TA$_{25}$ from each tensile test.

	PGS			PGS-TA$_{25}$		
Cure Condition	Strain, %	UTS, kPa	E, kPa	Strain, %	UTS, kPa	E, kPa
150 °C 24 h	50	556	932	43	328	635
	48	457	805	67	369	597
	83	639	668	41	402	1003
	36	414	929	52	814	1464
	48	490	866	40	723	1633
Mean ± SD	53 ±18	511 ± 88	840 ± 109	49 ± 11	527 ± 224	1066 ± 472
150 °C 16 h	80	321	347	87	515	510
	69	313	386	81	485	522
	55	261	393	89	481	471
	71	381	444	84	460	539
Mean ± SD	69 ± 10	319 ± 49	392 ± 40	85 ± 3.5	485 ± 23	510 ± 29
150 °C 8 h	217	355	148	129	387	270
	305	493	158	161	453	257
	192	332	157	144	446	280
	173	403	216	204	322	220
	153	388	236	170	435	232
Mean ± SD	208 ± 59	394 ± 62	183 ± 40	162 ± 28	409 ± 55	252 ± 25
		PGS-TA$_{15}$				
150 °C 24 h	54	652	1112			
	63	602	903			
	46	529	1076			
	46	578	1170			
	45	496	1026			
Mean ± SD	51 ± 7.7	571 ± 61	1057 ± 101			

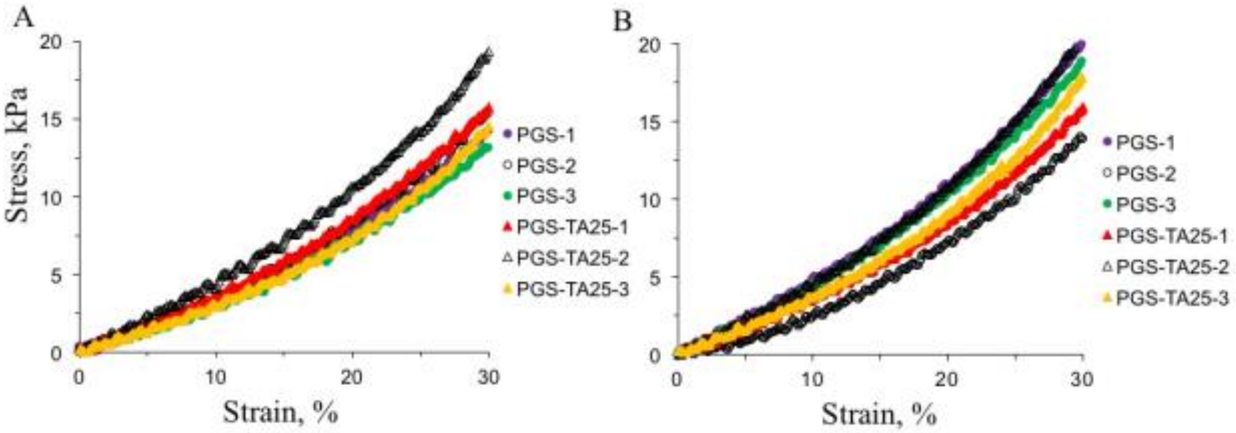

Fig. S6 Stress-strain curves of the compressive tests of the PGS control and PGS-TA_{25} porous scaffolds. (A) Before incubation and (B) incubation in PBS (1×, pH 7.4) at 37 °C for 75 h. The test for each sample was replicated three times (n=3) to obtain an average compressive modulus with standard deviation. The compressive modulus was determined according to the slope of the stress-strain curve between 5 - 20% strain.

4. FT-IR spectroscopy to examine the change of hydroxyl groups before and after a thermal crosslinking of PGS, PGS-TA$_{15}$ and PGS-TA$_{25}$

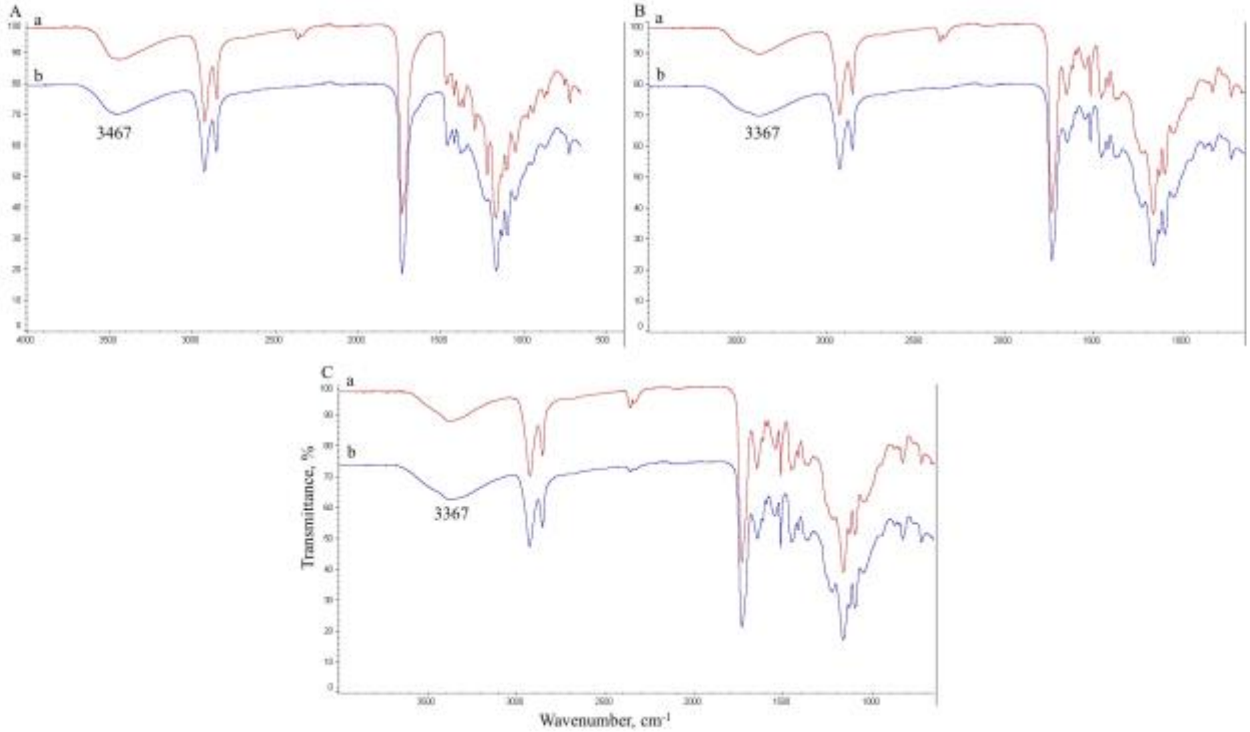

Fig. S7 Comparison of FT-IR spectra before and after a thermal crosslinking. (A) PGS control, (B) PGS-TA$_{15}$ and (C) PGS-TA$_{25}$. (a) Before and (b) after the thermal crosslinking was performed at 150 °C for 24 h under reduced pressure. The absorption bands at 3467 and 3367 cm^{-1} are attributed to secondary hydroxyl groups in PGS control and phenolic hydroxyl groups in PGS-TA polymers. The results show that the absorption intensity of the hydroxyl groups is nearly identical before and after the thermal crosslinking, indicating that most hydroxyl groups remain intact after the thermal crosslinking. These free secondary hydroxyl groups and phenolic hydroxyl groups form physical interactions and contribute to the elasticity of the crosslinked PGS and PGS-TA elastomers.