## **Supporting Information**

## Introduction of reversible urethane bond based on vanillyl alcohol for efficient self-healing of polyurethane

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	Temperature (°C)					
Sample code	5% T <sub>d</sub> *1	10% T <sub>d</sub> *1	T <sub>gs</sub> * <sup>2</sup>	T <sub>flow</sub> * <sup>2</sup>		
Control PU	311	331	-29	148		
VA10	303	317	-31	133		
VA20	301	316	-25	129		
VA30	300	315	-17	129		
<b>VA40</b>	298	315	-9	125		
VA40-5	297	313	-14	131		
VA40-10	295	313	-20	127		

Table S1. Thermal properties of synthesized PUs.

 $\ast^1\,T_d$  was measured by TGA

\*2  $T_{gs}$  and  $T_{flow}$  were measured by DMA

	Relaxation time (s)					Activation energy
Sample code	120 °C	130 °C	140 °C	145 °C	150 °C	(kJ/mol)
Control PU	-	-	539	241	98	247.6
VA10	-	220	71	-	33	134.6
VA20	-	315	102	-	38	149.9
VA30	-	380	120	-	45	151.2
VA40	-	614	162	-	55	171.1
VA40-5	408	147	65	-	-	124
VA40-10	294	114	59	-	-	108.5

Table S2. Relaxation time and activation energy of synthesized PUs.

Sample code	Tensile stre		
	Before healing	After healing	- Healing efficiency (%)
<b>Control PU</b>	25.5	17.7	69.3
VA10	29.5	17.8	60.5
VA20	32.8	16.6	50.7
VA30	35.7	15.3	42.9
<b>VA40</b>	37.2	12.1	32.4
VA40-5	18.4	16.3	88.4
VA40-10	14.9	14.4	96.5

Table S3. Tensile strength and healing efficiency of synthesized PUs at 140  $^\circ\mathrm{C}$  for 30 min.



Figure S1. Synthesis of m-CE.



Figure S2. FT-IR spectra of VA-based PUs.



Figure S3. FT-IR spectra of model structure for reversible urethane bond at elevated temperature.



Figure S4. SAXS profile of VA-based PUs.



Figure S5. TGA thermograms of VA-based PUs.



Figure S6. DMA thermograms of VA-based PUs.



Figure S7. Stress-relaxation curves of the VA-based PUs at various temperatures.



Figure S8. DSC thermograms of VA-based PUs.



Figure S9. Stress-strain curves of VA-based PUs.



Figure S10. Images of self-healing test specimens for VA40-10.



Figure S11. Tensile properties of PUs after repeated healing at 140  $\,\,^\circ\!\mathrm{C}.$ 



Figure S12. FT-IR spectra of DEA, BGE and m-CE.



Figure S13. NMR spectrum of m-CE.