Reprocessable polyurethane elastomers based on reversible ketal exchange: Dielectric properties and water resistance

Jianrong Dong[1], Hongye Yan[1]*, Xinhai Lv[1], Zhenbang Wang[1], Zixuan Rao[1], Bailin Zhu[2], Jun Wu[2], Yu Zhou[1], Hongxiang Chen[1,3,]*

[1] *School of Chemistry and Chemical Engineering, Wuhan University of Science and Technology, Wuhan 430081, China*

[2] *The State Key Laboratory of Refractory and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, China*

[3] *Key Laboratory of Catalysis and Energy Materials Chemistry of Ministry of Education & Hubei Key Laboratory of Catalysis and Materials Science, South-Central University for Nationalities，Wuhan 430074, China*

Corresponding author.
E-mail address: hyyan@wust.edu.cn
E-mail address: chenhx_916@hotmail.com; chenhongxiang@wust.edu.cn

Supplementary information

1. Exchange reaction of ketal-containing model compounds

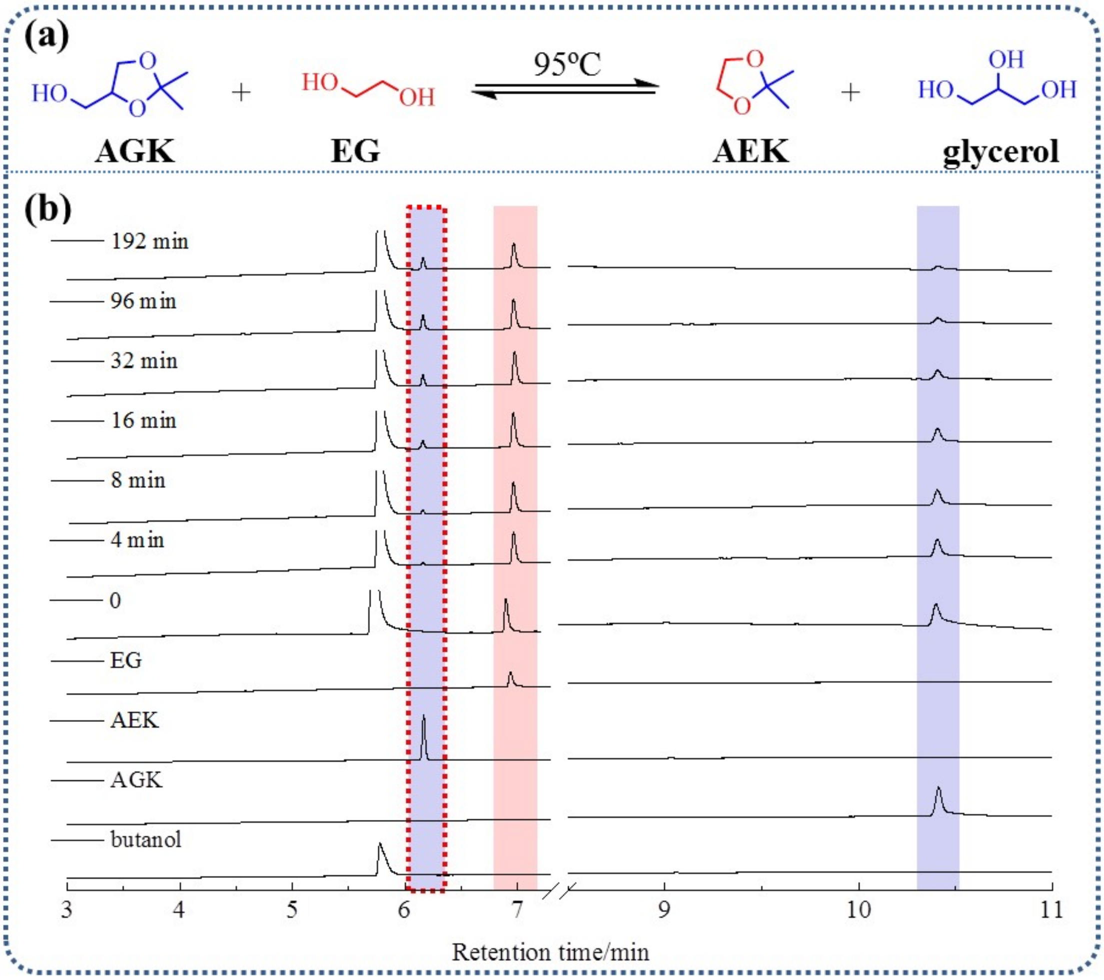


Figure S1 (a) Schematic diagram of exchange reaction between AGK and EG; (b) Gas chromatography of reaction mixtures at different time scales

2. ¹H NMR spectra of reaction mixture

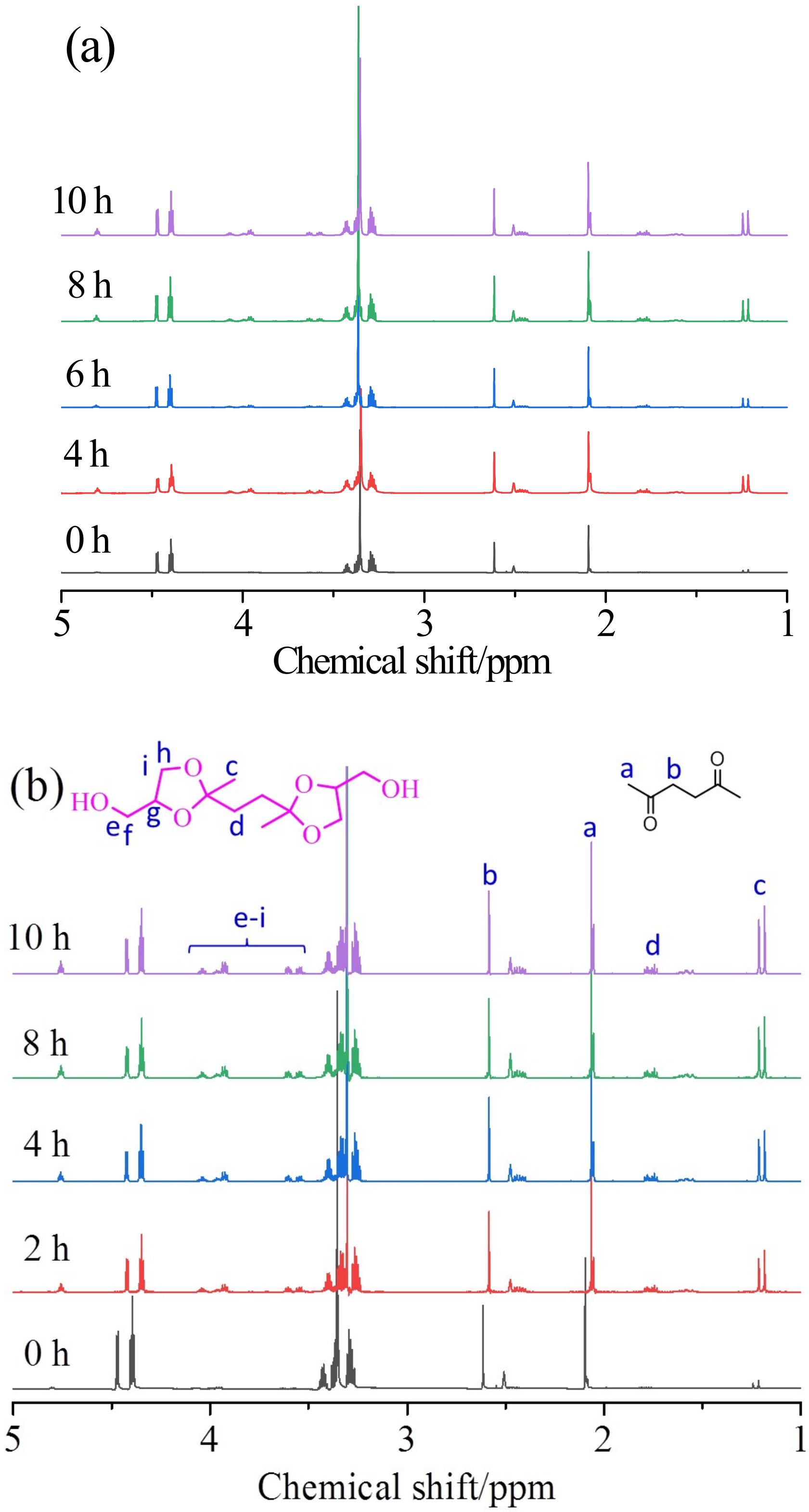


Figure S2 ¹H NMR spectra of reaction mixture of HDO and glycerol at different time scales: (a) 80 ºC; (b) 90 ºC

3. FTIR spectra of reaction mixture

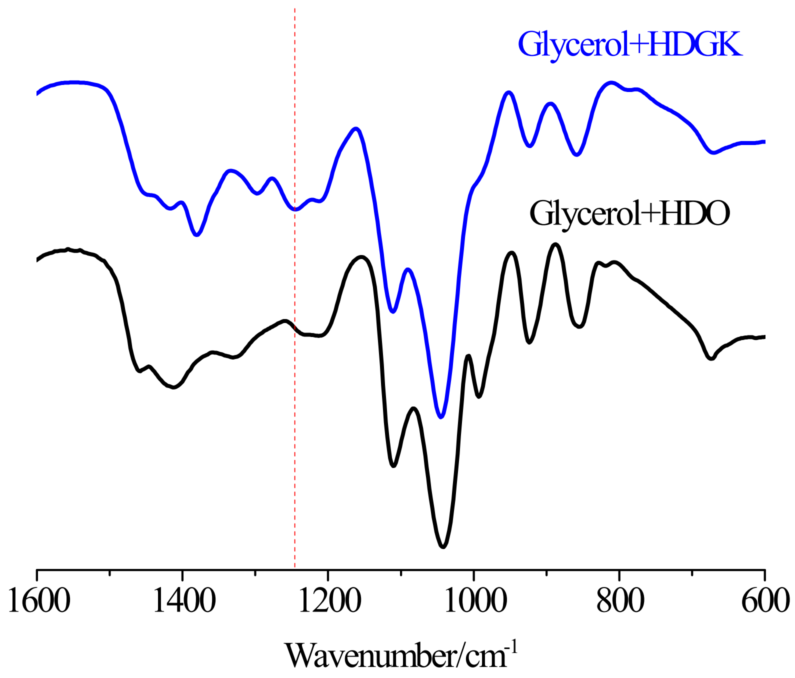


Figure S3 FTIR spectra of the filtrate after 11 h of reaction, the mixture of glycerol and 2,5-hexadione

4. Index of hydrogen bonding for polyurethane networks

Table S1 Bands, absorbance ratio of C=O stretching vibration, and index of hydrogen bonding (X_B) for polyurethane networks

Samples	Free C=O	Bonded C=O	A_F/A_B	X_B
KCPU-0	1731	1708	0.43	0.68
KCPU-1	1732	1710	0.26	0.78
KCPU-2	1732	1709	0.21	0.81
KCPU-3	1732	1709	0.25	0.78
KCPU-4	1733	1711	0.31	0.74

5. Tensile strength, elongation at break, and Young's modulus of KCPU-*x*

Table S2 Tensile strength, elongation at break, Young's modulus, and healing efficiency of samples before and after healing at 100 ºC for 5 h

Samples	Original samples			Healed samples			η/%
	σ/MPa	ε/%	E/MPa	σ/MPa	ε/%	E/MPa	
KCPU-0	8.04±2.39	673±41	3.0±0.4	1.70±0.42	221±165	1.7±0.3	21.1
KCPU-1	11.79±0.79	724±80	5.0±0.5	1.81±0.18	147±18	4.4±0.6	15.4
KCPU-2	10.01±1.10	620±55	6.8±1.0	2.79±0.09	414±15	5. 6±0.4	27.8
KCPU-3	9.78±1.45	596±67	3.8±0.2	4.86±0.37	424±58	3.7±0.9	49.6
KCPU-4	5.30±0.51	617±137	3.2±0.6	3.54±0.34	509±61	3.0±0.5	66.7

σ is the tensile strength, ε is the elongation at break, and E is the Young's modulus.

6. Contact angles of KCPU-*x*

Table S3 Advancing angles and Receding angles of KCPU-*x*

Contact angle	KCPU-0	KCPU-1	KCPU-2	KCPU-3	KCPU-4
Advancing angle	99.3±0.8	93.3±0.6	96.5±0.8	95.5±0.5	102.8±1.3
Receding angle	101.0±1.2	94.3±2.5	97.5±1.4	95.7±1.1	102.5±1.1

7. Comparison of KCPU-4 and other dielectric elastomers in the literature

Table S4 Dielectric constant, dielectric loss, and dielectric loss factor of acrylic and silicone elastomers in the literature

Dielectric Elastomers	Polymers	Dielectric properties at 10^3 Hz			Reference
		ε'	ε''	tan δ	
PMMA-3	Acrylic polymer	4.3	0.044	0.01	1
MBM 104 TPEGs	Acrylic polymer	4.6			2
VHB 4905	Acrylic polymer	4.7			3
Wacker Elastosil® 2030/20	siloxane	2.8			3
BDDA	siloxane	4.6	0.1	0.022	4
Si-B_IN30	siloxane	4.3	0.047	0.011	5
TC5005-40	siloxane	4.4	0.11	0.025	6

Table S5 Dielectric constant, dielectric loss, dielectric loss factor, and reprocessing temperature of polyurethane elastomers in the literature and KCPU-4 in this work

Dielectric Elastomers	Dielectric properties at 10^3 Hz			Reprocessing temperature/ºC	Reference
	ε'	ε''	tan δ		
6FDA-15-A	1.5	0.023	0.015	-	7
PU(26 h RT-cure in dried air)	3.2	0.202	0.063	-	8
PU(end of RT-cure)	3.0	0.45	0.15	-	9
PPG-MDI-TMP	8.6	1.032	0.12	-	10
p(BA-HEA)@MDI-1	7.1	0.284	0.04	-	11
Polyether-HDI-BD	8.1	0.203	0.025	-	12
PDET-MDI-BD	1.5	0.03	0.02	-	13
PU1400	7.0	0.7	0.1	-	14
BPU3	7.5	0.338	0.045	-	15
PU-41.03% PVP	5.5	0.385	0.07	-	16
Soybean Polyol-MDI	6.1	0.549	0.09	-	17
Polyol-MDI-Gly-BD	5.0	0.6	0.12	-	18
PU702	7.2	1.512	0.21	-	19
Polyether-HDI-CO-BD	10.2	1.02	0.1	-	20
Capa™2085	8.9	0.712	0.08	-	21
PU-7LNP	20.0	4.4	0.22	120	22
KCPU-4	**11.9**	**0.536**	**0.045**	**95**	**This work**

ε', Dielectric constant; ε'', dielectric loss; tan δ, dielectric loss factor.

8. Stress relaxation of KCPU-*x* at different temperatures

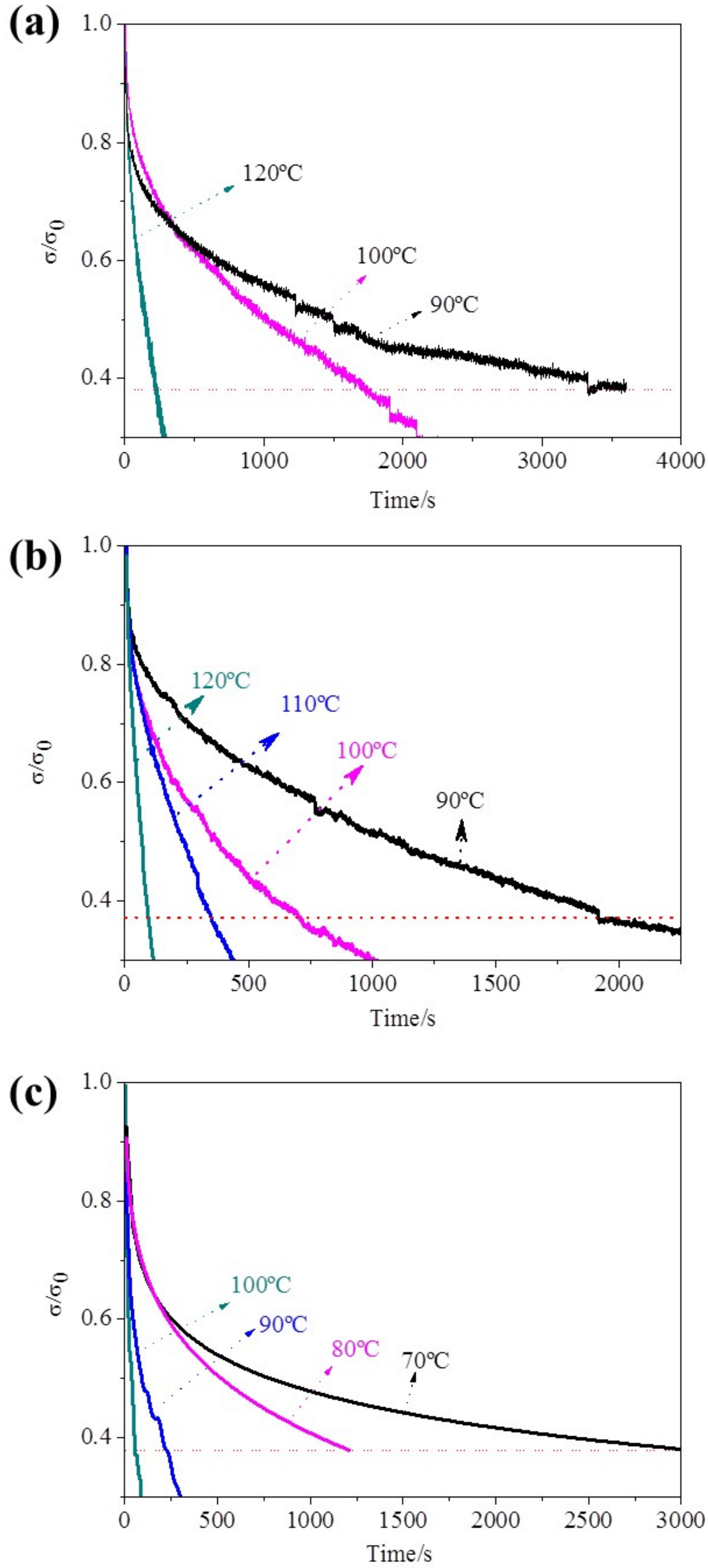


Figure S4 Stress relaxation curves of samples at different temperatures: (a) KCPU-1, (b) KCPU-2, (c) KCPU-4

9. Difference in the gauge length before and after stress relaxation

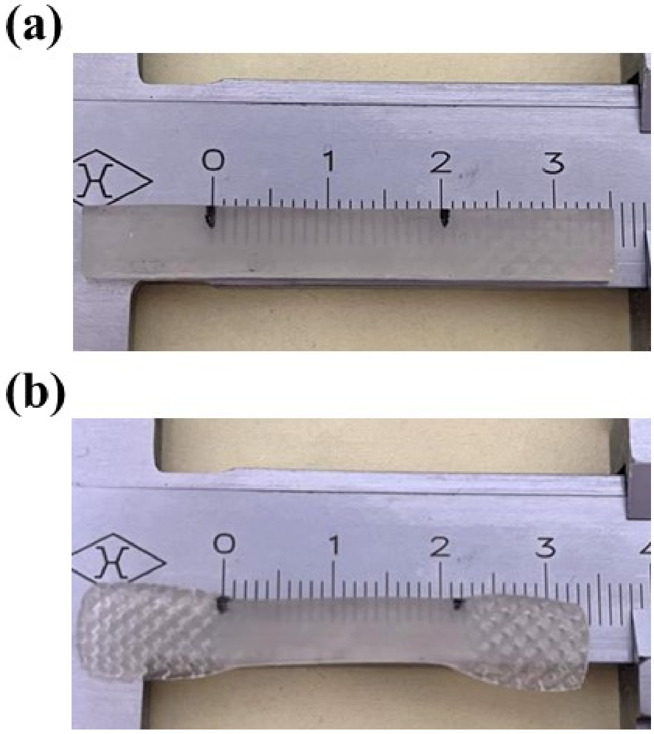


Figure S5 Length difference between two marked points: (a) the original KCPU-3 and (b) the cooled KCPU-3 after stress relaxation at 90 ºC

10. Stress-strain curves of KCPU-*x* for three cyclic loading at high temperature

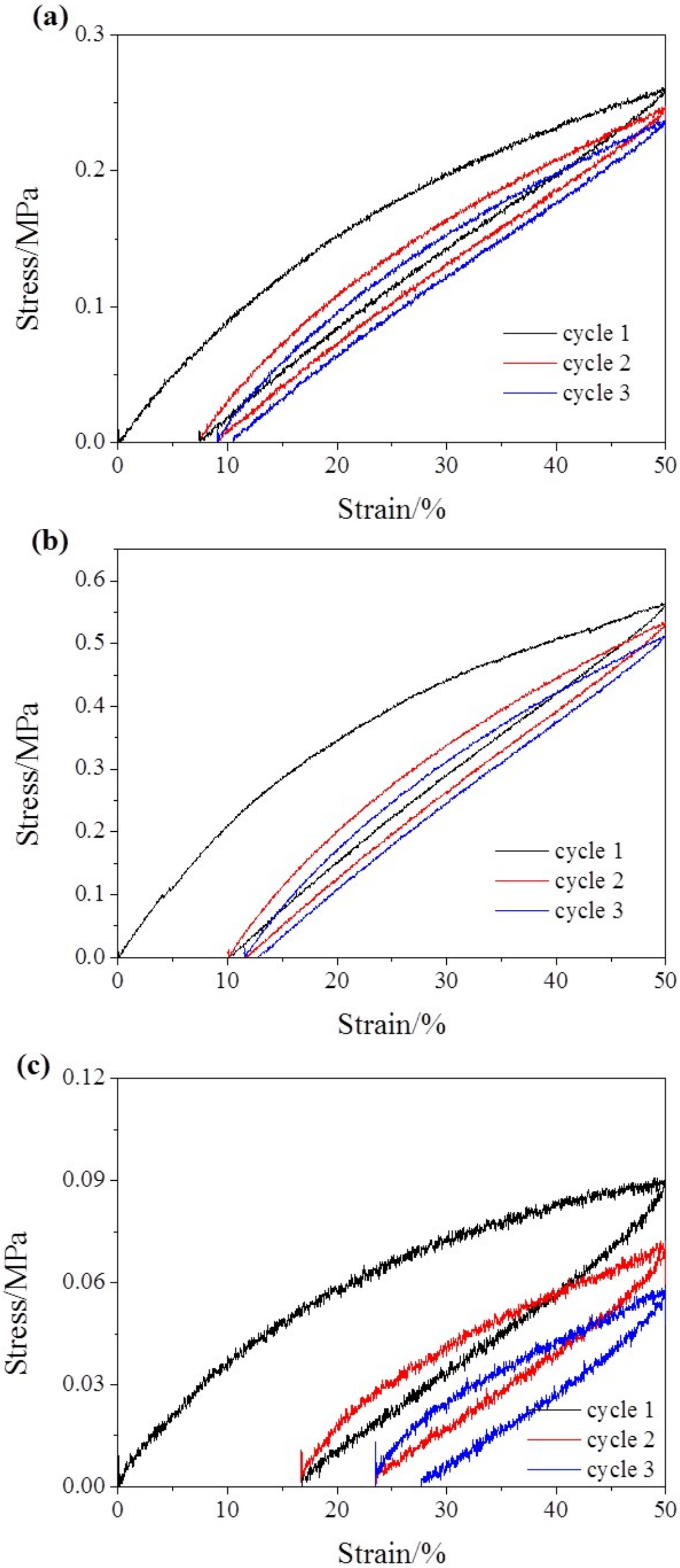


Figure S6 Stress-strain curves for three cyclic loading at 100 ºC: (a) KCPU-1, (b) KCPU-2, and (c) KCPU-4

11. Stress-strain curves of KCPU-*x* for three cyclic loading at high temperature

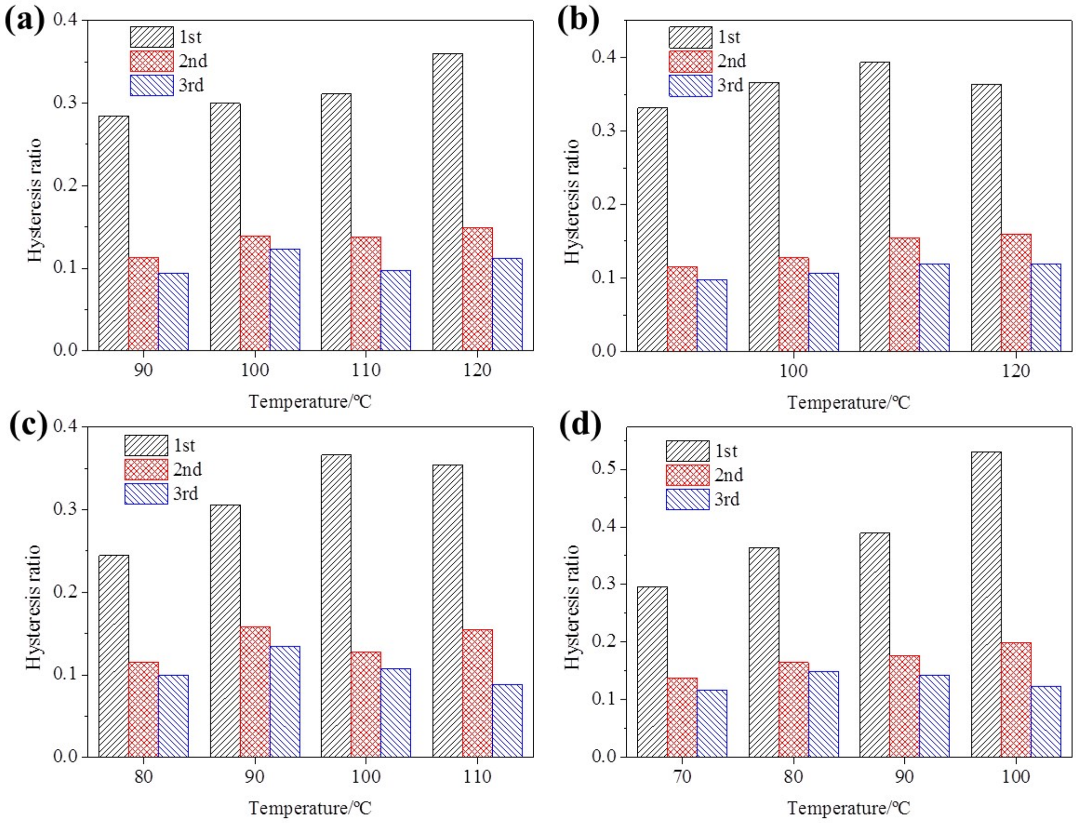
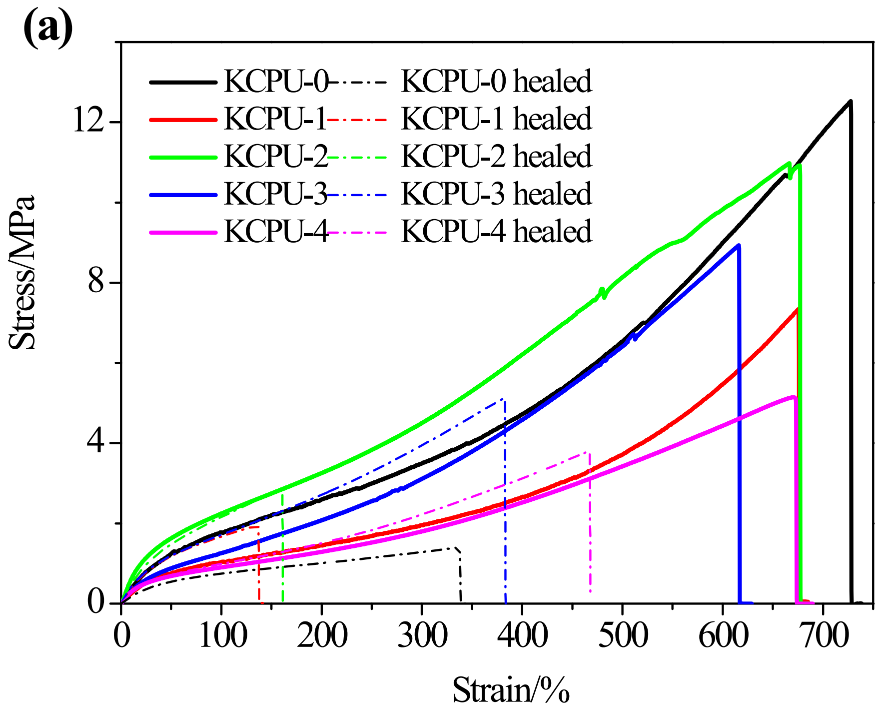


Figure S7 Temperature dependence of hysteresis loop area at different load-unload cycles: (a) KCPU-1, (b) KCPU-2, (c) KCPU-3, and (d) KCPU-4

12. Healing of KCPU-*x*



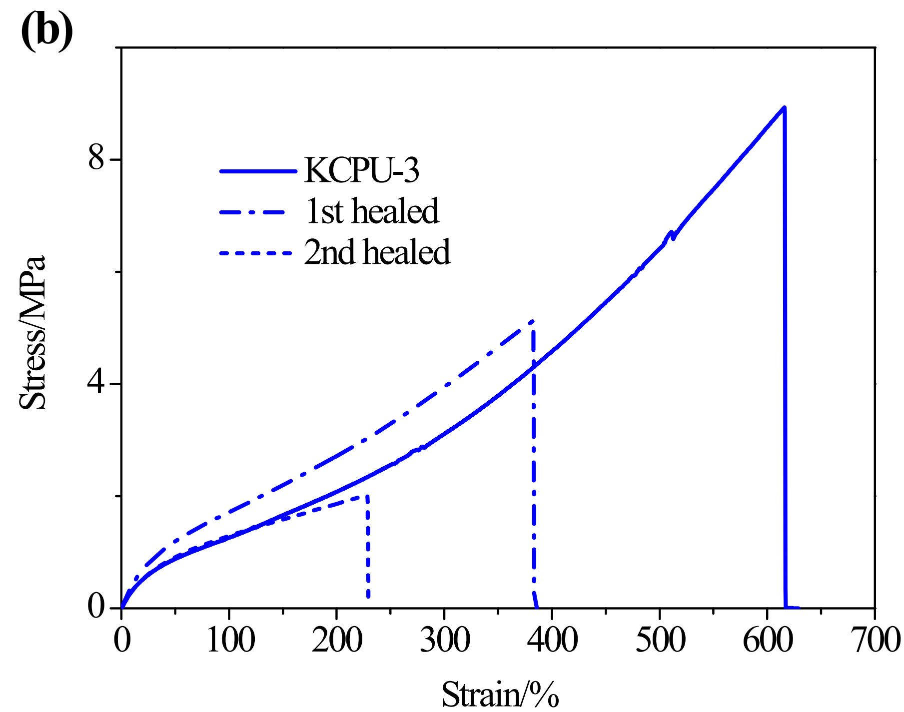


Figure S8 (a) Stress-strain curves of original and healed KCPU-*x*, (b) Stress-strain curves of KCPU-3 after repetitive healing experiments

13. Recovery efficiency of reprocessing samples

Table S6 Reprocessing temperature and recovery efficiency of KCPU-*x* samples in the tensile strength and elongation at break

Samples	Temperature of reprocessing/°C	Recovery efficiency of tensile strength/%	Recovery efficiency of elongation at break/%
KCPU-0	140	40.3±2.1	51.1±10.5
KCPU-1	120	24.3±0.8	33.8±2.5
KCPU-2	110	35.8±4.6	31.5±5.2
KCPU-3	100	23.8±1.7	39.7±3.5
KCPU-4	95	74.7±2.3	69.4±2.4

References

1. J. Chen, Y. Wang and W. Chen, *J. Mater. Chem. C*, **2021**, 9, 5000-5007.
2. P. H. Vargantwar, A. E. Özçam, T. K. Ghosh, and R. J. Spontak, *Adv. Funct. Mater.*, **2012**, 22, 2100-2113.
3. F. B. Albuquerque and H. Shea, *Smart Mater. Struct.*, **2019**, 28, 075042.
4. A. Chortos, E. Hajiesmaili, J. Morales, D. R. Clarke and J. A. Lewis, *Adv. Funct. Mater.*, **2020**, 30, 1907375.
5. F. B. Madsen, L. Yu and A. L. Skov, *ACS Macro Lett.*, **2016**, 5, 1196-1200.
6. F. Galantini, F. Carpi and G. Gallone, *Smart Mater. Struct.*, **2013**, 22, 104020.
7. Y. Li, B. Ma, R. Zhang and X. Luo, *Polymer*, 2022, **253**, 125035.
8. B. Zimmer, C. Nies, C. Schmitt, C. Paulo and W. Possart, *Polymer*, 2018, **149**, 238-252.
9. B. Zimmer, C. Nies, C. Schmitt and W. Possart, *Polymer*, 2017, **115**, 77-95.
10. S. Desai, I.M. Thakore, B.D. Sarawade and S. Devi, *Eur. Polym. J.,* 2000, **36**, 711-725.
11. Y. Zhao, J. Zha, L. Yin, S. Li, Y. Wen and Z. Dang, *Polymer*, 2018, **149**, 39-44.
12. S. Oprea, O. Potolinca and V. Oprea, *High Perform. Polym.*, 2011, **23**, 49-58.
13. A. Marcos-Fernandez, R. Navarro, E. Benito, J. Guzman and L. Garrido, *Eur. Polym. J.*, 2021, **155**, 110576.
14. K. Raftopoulos, B. Janowski, L. Apekis, K. Pielichowski and P. Pissis, *Eur. Polym. J.,* 2011, **47**, 2120-2133.
15. S. Oprea, *J. Polym. Res.*, 2011, **18**, 1777-1785.
16. L. V. Karabanova, G. Boiteux, O. Gain, G. Seytre, L. M. Sergeeva, E. D. Lutsyk and P. A. Bondarenko, *J. Appl. Polym. Sci.*, 2003, **90**, 1191-1201.
17. A. Zlatanic, C. Lava, W. Zhang and Z. S. Petrovic, *J. Polym. Sci. B,* 2004, **42**, 809-819.
18. S. Oprea, V. Musteata and V. O. Potolinca, *J. Elastomers Plast.*, 2011, **43**, 559-575.
19. Z. S. Petrovic, I. Javni and G. Banhegy, *J. Polym. Sci. B*, 1998, **36**, 237-251.
20. S. Oprea, *J. Appl. Polym. Sci.*, 2011, **119**, 2196-2204.
21. M. Zajac, H. Kahl, B. Schade, T. Rodel, M. Dionisio and M. Beiner, *Polymer*, 2017, **111**, 83-90.
22. G. Qi, W. Yang, D. Puglia, H. Wang, P. Xu, W. Dong, T. Zheng and P. Ma, *Mater. Des.*, 2020, **196**, 109150.