Supporting Information For

A wear-resistant, self-healing and recyclable multifunctional waterborne polyurethane coating with mechanical tunability based on hydrogen bonding and aromatic disulfide structure

Chao Liu[a] *, Qing Yin[b], Qiming Yuan[b], Lifen Hao[b], Lei Shi[c], Yan Bao[d], Bin Lyu[d], Jianzhong Ma[d] *

[a] *Shaanxi Collaborative Innovation Center of Industrial Auxiliary Chemistry and Technology, Shaanxi University of Science &Technology, Xi'an 710021, China*

[b] *College of Chemistry and Chemical Engineering, Shaanxi University of Science & Technology, Xi'an 710021, China*

[c] *Zhejiang Hexin Science and Technology Co., Ltd, Jia Xing 314003, China*

[d] *College of Bioresources Chemical and Materials Engineering, Shaanxi University of Science & Technology, Xi'an 710021, China*

* Corresponding authors.
E-mail address: lc1010158@163.com (C. Liu), majz@sust.edu.cn (J. Ma).

1.

Preparation of 5-(2-hydroxyethyl)-6-methyl-2-aminuracil (HMA). HMA was obtained using the following route (Scheme 1). Guanidine carbonate (7.23 g, 40 mmol) and α-acetyl-γ-butyrolactone (5.13 g, 40 mmol) were refluxed in absolute ethanol (50 mL) for 10 h in the presence of TEA (15 mL) at 80°C. Then, the mixture was filtered and washed with ethanol absolute for several times. Finally, a white power of HMA was prepared after vacuum drying at 60°C.

α-acetyl-γ-butyrolactone   **Guanidine carbonate**   **HMA**
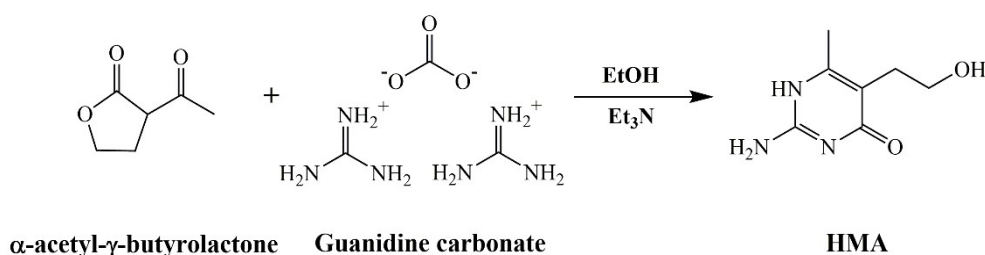
Scheme S1. Synthesis route of HMA.

Wear-resistance test. The HSPU emulsion was applied in leather coating, and the coated leather was cut into to annular samples with an outer diameter of 12 cm and inner diameter of 6.5 cm. The wear resistance of coated leather samples was tested by GB/T1768-2006 method with a Gotech Taber machine (Taiwan, China). Briefly, the weights of samples were weighed. Then, the samples were placed in the Taber machine and wear for 50 cycles. Finally, the weights of worn leather samples were weighed. Each kind of samples was examined three times [1]. The wear index was calculated according to the Formula (1):

$$\text{wear index (mg)} = \frac{\text{wear loss mass}}{\text{test rotation number (50 r)}} \times 100 \qquad (1)$$

[1] L.F. Wei, J.Z. Ma, W.B. Zhang, C. Liu, Y. Bao, The tribological behaviors of polyacrylate/graphene oxide and polyacrylate/surfactant-modified reduced graphene oxide composite coatings on flexible leather substrates, Prog. Org. Coat. 122 (2018) 64-71.

2.

Chemical Structure of HMA. The chemical structure of HMA was acquired by FT-IR spectra (Fig. S1) and ^1H NMR spectrum (Fig. S2). As shown in Fig. S1, there is an absorption peak at 3377 cm^{-1} which is owning to the stretching vibrations of O-H [2]. The peaks at 3124 and 1558 cm^{-1} attribute to the stretching vibration and deformation vibration absorption of N-H [3, 4]. The bonds at 2959 and 1398 cm^{-1} respectively assign to the stretching and bending vibrations of -CH$_3$ groups [5, 6]. The four clear absorption peaks at 1665, 1602, 1237 and 1050 cm^{-1} correspond to stretching vibrations of C=O, C=C, C-N and C-O, respectively [7]. All these results demonstrate that HMA has been obtained successfully. As presented in Fig. S2, the chemical shifts of hydrogen atoms in HMA are 8.32-2.09 ppm: 8.32 (s, 1H, -N*H*-(C=O)-NH$_2$), 6.50 (s, 2H, -NH-(C=O)-N*H*$_2$), 4.78 (s, 1H, -CH$_2$O*H*), 3.36 (t, 2H, -C*H*$_2$CH$_2$OH), 2.45 (t, 2H, -CH$_2$C*H*$_2$OH), 2.09 (s, 3H, =C(C*H*$_3$)), confirming that HMA has the expected structure.
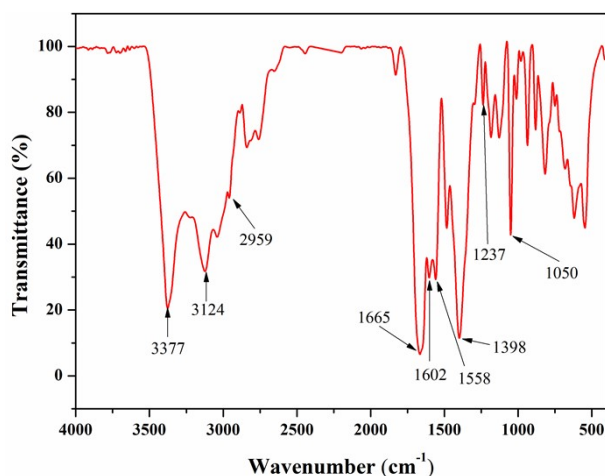

Fig. S1. FT-IR spectra of HMA.
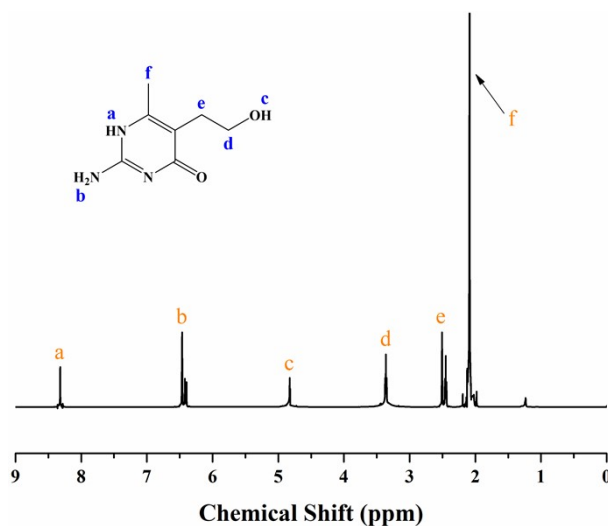
Fig. S2. ^{1}H NMR spectra of HMA.

[2] Y. Yang, Z.S. Ye, X.X. Liu, J.H. Su, A healable waterborne polyurethane synergistically cross-linked by hydrogen bonds and covalent bonds for composite conductors, J. Mater. Chem. C 8 (2020) 5280-5292.

[3] Z.Y. Yang, D.C. Sun, Self-healing supramolecular waterborne polyurethane dispersions with quadruple hydrogen bonds in main chain, J. Appl. Polym. Sci. 137(45) (2020) 49413.

[4] J. Choi, S. Kim, J. Yoo, S. Choi, K. Char, Self-healable antifreeze hydrogel based on dense quadruple hydrogen bonding, Macromolecules 54(13) (2021) 6389-6399.

[5] X. Huang, Y. C. Zhao, B. H. Han, Supramolecular organic network assembled from quadruple hydrogen-bonding motifs, Chem. Commun. 52 (2016) 6597-6600,.

[6] M. M. Zhai, Q. Chen, W. Yuan, Q. X. Shi, H. Xu, Directional self-assembly of gold nanorods into 1D and 2D arrays by quadruple hydrogen bonding, Mater. Chem. Front. 3 (2019) 1888-1891.

[7] K. Liu, L. Cheng, N.B. Zhang, H. Pan, X.W. Fan, G. F. Li, Z. M. Zhang, D. Zhao, J. Zhao, X. Yang, Y. M. Wang, R. X. Bai, Y. H. Liu, Z. Y. Liu, S. Wang, X. L. Gong, Z. N. Bao, G. Y. Gu, W. Yu, X. Z. Yan, Biomimetic impact protective supramolecular polymeric materials enabled by quadruple H-bonding, J. Am. Chem. Soc. 143(2) (2021) 1162-1170.

3.

Particle size of HSPU emulsions. Fig. S3a shows the particle size distribution of HSPU emulsions with different HMA or APDS contents. It can be seen in Figure S3a that the average size of all HSPU emulsion particles ranged from 28.49 to 116.7 nm, with a narrow particle size distribution. After being left at room temperature for 6 months, the particle size of the HSPU-7 emulsion almost kept constantly (Fig. S3b). Therefore, the prepared HSPU emulsions have excellent emulsion stability, which can guarantee their further applications as self-healing materials.
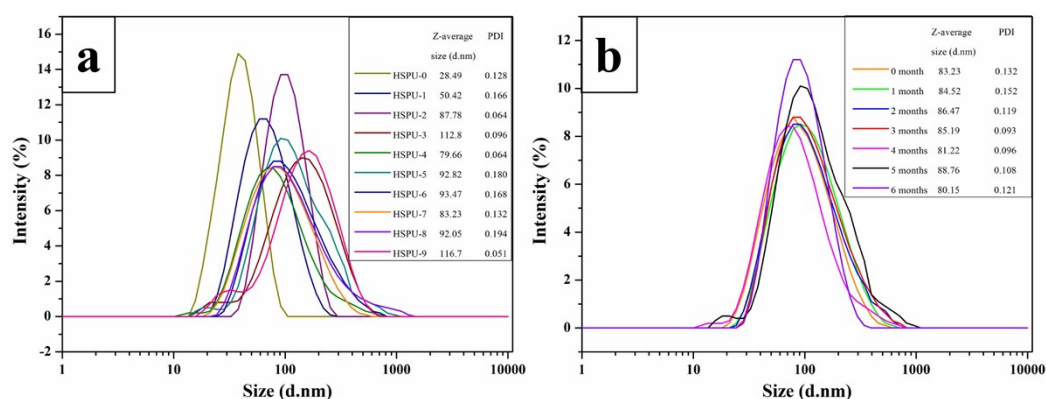
Fig. S3 Particle size distribution of (a) HSPU emulsion particles with different HMA or APDS contents and (b) HSPU-7 emulsion particles with different storage time.

4.

Table S1. Mechanical properties of various HSPU films

Samples	Tensile stress (MPa)	Elongation at break (%)
HSPU-0	5.82	636.65
HSPU-1	15.21	808.23
HSPU-2	17.42	991.8
HSPU-3	21.11	916.3
HSPU4	19.87	584.94
HSPU-5	24.8	516.3
HSPU-6	29.67	428.7
HSPU-7	17.58	698.17
HSPU-8	20.35	660.97
HSPU-9	18.99	788.95

5.

Table S2. Self-healing efficiency of HSPU-9 film with different healed time at room temperature

	Original	Healed for 4 h	Healed for 6 h	Healed for 8 h	Healed for 10 h
Tensile stress (MPa)	18.99	7.79	13.49	18.05	17.96
Healing efficiency (%)	——	41	71	95.1	94.6

Table S3. Self-healing efficiency of HSPU-9 film healed at different temperatures for 30 min

	Original	Healed at 20°C	Healed at 50°C	Healed at 80°C
Tensile stress (MPa)	18.99	3.17	16.96	18.72
Healing efficiency (%)	——	16.7	89.3	98.6

6.

Table S4. Self-healing efficiencies of HSPU-0~HSPU-6 and HSPU-9 films at room temperature under different healing times

Samples	Tensile strength/MPa	Self-healing efficiency/% (RT, 4h)	Self-healing efficiency/% (RT, 6h)	Self-healing efficiency/% (RT, 8h)
HSPU-0	5.82	8.11	15.7	19.2
HSPU-1	15.21	38.3	49.2	58.6
HSPU-2	17.42	52.4	61.8	72.4
HSPU-3	21.11	56.1	70.5	79.2
HSPU-4	19.87	30.1	55.4	75.4
HSPU-5	24.8	24.9	68.4	90.2
HSPU-6	29.67	16.5	61.7	85.7
HSPU-9	18.99	41.1	71.3	95.1

In order to explore the effect of the introduction of UPy and aromatic disulfide monomers on the self-healing efficiency of HSPU films, the self-healing efficiencies of HSPU-0~HSPU-6 and HSPU-9 films at room temperature under different healing times were studied (As shown in table S4). Without the introduction of UPy and aromatic disulfide, HSPU-0 also showed a certain self-healing function. This is mainly attributed to the fact that HSPU-0 structure contains a large number of hydrogen bonds, which endow it with certain self-healing function. It can be seen from Table S4 that when the healing time is 4 h, the self-healing efficiencies of HSPU films containing UPy monomer are significantly better than those of HSPU films containing aromatic disulfide monomer. This may be attributed to the lower bond energy of hydrogen bonds compared to aromatic disulfide bonds, so they can dissociate and recombine rapidly, resulting in a higher self-healing efficiency of the film in a shorter time [8]. However, when the healing time is extended to 8 h, the self-healing efficiencies of HSPU films containing aromatic disulfide monomers are significantly better than those of HSPU films containing the same ratio of UPy monomers. This may be attributed to the fact that the bond energy of the aromatic disulfide bond is higher than that of the quadruple hydrogen bond, so it can fully dissociate and recombine under a longer repair time, so that the film obtains a higher self-healing efficiency [9]. It is worth noting that the self-healing efficiency of HSPU-9 is significantly higher than those of HSPU films containing only UPy or aromatic disulfide monomers after 8 h of healing. This may be attributed to the fact that the dissociation and reorganization of the quadruple hydrogen bonds can accelerate the movement

of the HSPU molecular chain and further promote the cleavage and reorganization of aromatic disulfide bonds. Therefore, the molecular chains are sufficiently diffused and contacted, which provides convenient conditions for the synergic interaction of UPy and aromatic disulfide bonds, thus improving the self-healing efficiency of HSPU [10].

[8] J. Ye, G. H. Lin, Z. Q. Lin, H. Y. Deng, J. J. Huang, H. P. Xiang, M. Z. Rong, M. Q. Zhang, UV-curable polyurethane elastomer with UV-irradiation/thermo dual-activated self-healability, Macromol. Mater. Eng., 2022, 307(6): 2100874.

[9] Y. Zhang, J. Zheng, W.L. Ma, X. Zhang, Y. Q. Du, K. Li, Y. H. Liu, G. B. Yu, Y. F. Jia, Ultra-stretchable and ultra-low temperature self-healing polyurethane enabled by dual dynamic bonds strategy, React. Funct. Polym., 2022, 178: 105364.

[10] J. C. Rong, J. Zhong, W. L. Yan, M. C. Liu, Y. L. Zhang, Y. L. Qiao, C. Q. Fu, F. Gao, L. Shen, H.F. He, Study on waterborne self-healing polyurethane with dual dynamic units of quadruple hydrogen bonding and disulfide bonds-ScienceDirect, Polymer, 2021, 221(14): 123625.