

# Synthesis and Characterization of Silver-Thiolate Dynamic Crosslinking Waterborne Polyurethane with Room-Temperature Self-Healing Property

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# Supporting Information

**Table S1.** Formulas for WPU-Ag.

Components (mol)	WPU-Ag-0.00	WPU-Ag-0.25	WPU-Ag-0.50	WPU-Ag-0.75	WPU-Ag-1.00
PPG-N210	0.400	0.400	0.400	0.400	0.400
DMPA	0.298	0.298	0.298	0.298	0.298
IPDI	1.080	1.080	1.080	1.080	1.080
BDO	0.370	0.370	0.370	0.370	0.370
TEA	0.223	0.223	0.223	0.223	0.223
AgNO <sub>3</sub>	0.000	0.019	0.037	0.056	0.075
H <sub>2</sub> O <sub>2</sub>	0.574	0.574	0.574	0.574	0.574

**Table S2.** Percentages of AgNO<sub>3</sub>, Ag<sub>2</sub>O, Ag in WPU.

Mass (g) / Percentage (wt%)	WPU-AgNO <sub>3</sub>	WPU-Ag <sub>2</sub> O	WPU-Ag
0.00	0.00/0.00	0.00/0.00	0.00/0.00
0.25	0.32/0.43	0.22/0.30	0.21/0.28
0.50	0.63/0.85	0.43/0.58	0.40/0.54
0.75	0.95/1.27	0.65/0.88	0.60/0.81
1.00	1.27/1.70	0.87/1.17	0.81/1.09

In WPU-Ag system, the -C=O peak could be attributed to the peaks of free -C=O, coordinated -C=O with Ag, and H-bonding -C=O. So the -C=O peak was split and fitted by Peakfit software and the fitting curves were shown in Figure S1. Fitting results were listed in Table S3. From Table S3, we could find that the peak area of -C=O coordinated with Ag was increased to the maximum value of 34.87% for WPU-Ag-0.5, and the peak position located at the lowest wavenumber 1722.09 cm<sup>-1</sup>, demonstrating that a large part Ag(0) easily coordinated with -C=O with the smaller excitation energy.

In WPU-Ag@S system, the -C=O peak could be attributed to the peaks of free -C=O, coordinated -C=O with Ag, and H-bonding -C=O. So the -C=O peak was split and fitted by Peakfit software and the fitting curves were shown in Figure S2. Fitting results were listed in Table S4. From Table S4, we could find that the peak area of -C=O coordinated with Ag was decreased to the minimum value of 11.97% for WPU-Ag@S-0.5, and the peak position located at the lowest wavenumber 1722.98 cm<sup>-1</sup>, demonstrating that small part Ag(0) were coordinated with -C=O with the smaller excitation energy. Moreover, this may be due to that a large part of Ag was coordinated with -SH to form the S-Ag coordinating bonds.

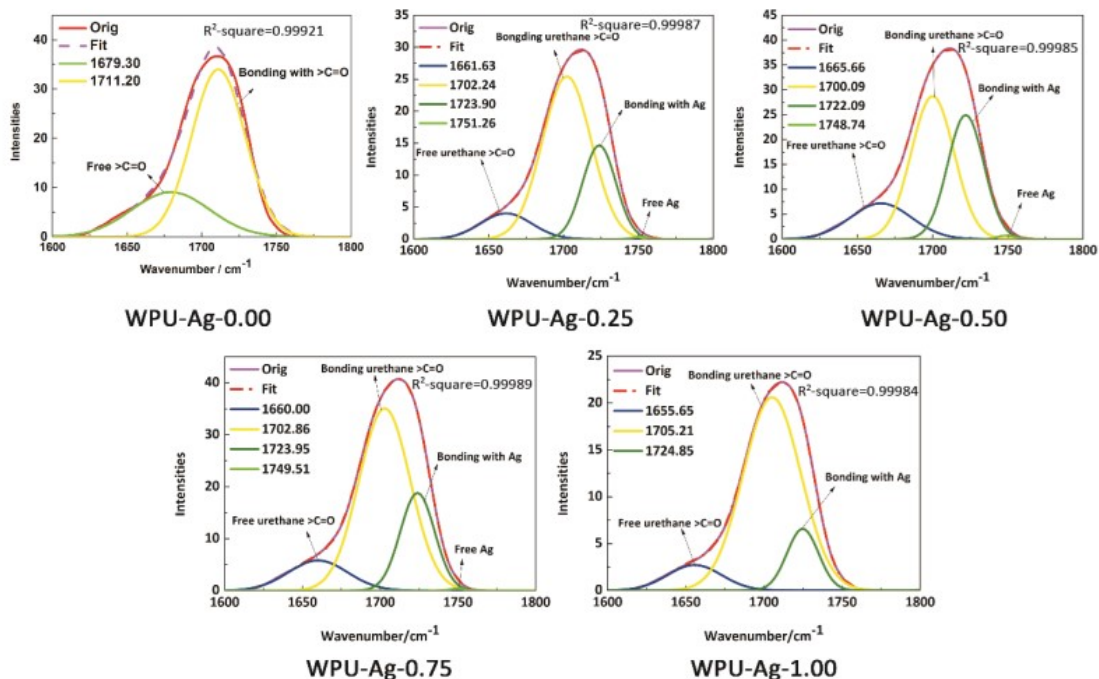


Figure S1. FTIR peak fitting curve of >C=O in WPU-Ag series.

Table S3. Peak fitting results of carbonyl >C=O in the WPU-Ag series.

Samples	Ag bonded with -C=O in urethane				Form H-bond with -C=O in urethane				H-bonding Index
	Free >C=O		coordination		H-bond		Free >C=O		
	$\nu/\text{cm}^{-1}$	Area(%)	$\nu/\text{cm}^{-1}$	Area(%)	$\nu/\text{cm}^{-1}$	Area(%)	$\nu/\text{cm}^{-1}$	Area(%)	
WPU-Ag-0.00	—				1711.00	88.68	1679.30	11.32	7.83
WPU- Ag-0.25	1751.26	0.29	1723.90	25.12	1702.24	63.98	1661.63	10.61	8.17
WPU- Ag-0.50	1748.74	0.45	1722.09	34.87	1700.09	47.72	1665.66	16.96	4.74
WPU- Ag-0.75	1749.51	0.20	1723.95	23.07	1702.86	64.41	1660.00	12.32	6.99
WPU- Ag-1.00	1750.76	0.00	1724.85	13.42	1705.21	77.06	1653.65	9.52	9.50

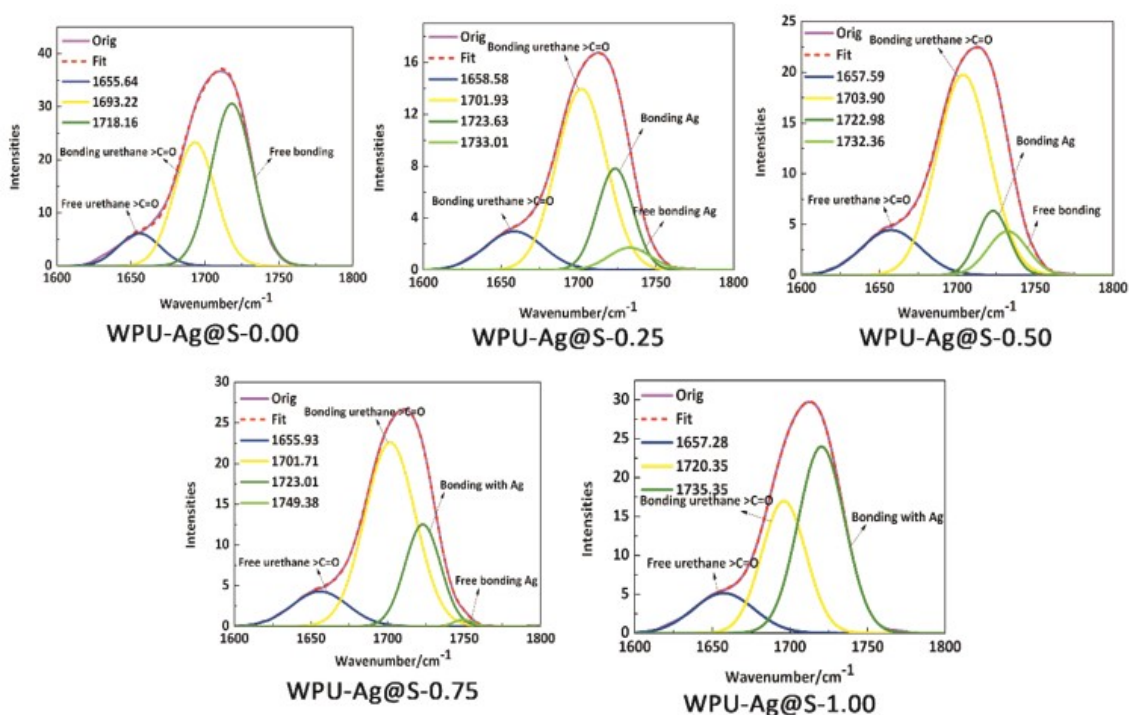


Figure S2. FTIR peak fitting curve of >C=O in WPU-Ag@S series.

**Table S4.** Peak fitting results of carbonyl>C=O in WPU-Ag@S series.

Samples	Ag bonded with -C=O in urethane				Form H-bond with -C=O in urethane				H-Bonding Index
	Free-C=O		Coordination		H-bond		Free-C=O		
	$\nu/\text{cm}^{-1}$	Area(%)	$\nu/\text{cm}^{-1}$	Area(%)	$\nu/\text{cm}^{-1}$	Area(%)	$\nu/\text{cm}^{-1}$	Area(%)	
WPU-Ag@S-0.00	—				1711.00	11.32	1679.30	88.68	7.83
WPU- Ag@S-0.25	1733.01	6.02	1723.63	22.77	1701.93	57.18	1658.58	14.03	3.99
WPU- Ag@S-0.50	1732.36	10.21	1722.98	11.97	1703.90	62.22	1657.59	15.60	2.87
WPU- Ag@S-0.75	1749.38	0.82	1723.01	24.20	1701.71	62.06	1655.93	12.93	6.27
WPU- Ag@S-1.00	1732.36	0.00	1720.35	51.18	1696.10	34.53	1657.28	14.29	6.00

**Table S5.** Tensile strength ( $\sigma$ ), elongation at break ( $\epsilon$ ), and self-healing efficiency ( $\eta_\sigma$ ,  $\eta_\epsilon$ ) for WPU-Ag@S series. at room temperature for 30 min.

Samples	$\sigma_s/\text{Mpa}$	$\sigma/\text{Mpa}$	$\eta_\sigma/\%$	$\epsilon_s/\%$	$\epsilon/\%$	$\eta_\epsilon/\%$
0.00	0.70	0.87	80.01	966.42	1277.63	75.64
0.25	0.66	0.74	88.84	1173.68	1215.81	96.53
0.50	1.25	1.27	98.69	1141.27	934.83	122.08
0.75	1.28	1.68	76.00	890.85	1113.65	80.00
1.00	1.51	2.35	64.14	739.75	1096.28	67.48

**Table S6.** Tensile strength ( $\sigma_s$ ), elongation at break ( $\epsilon_s$ ), and self-healing efficiency ( $\eta_\sigma$ ,  $\eta_\epsilon$ ) for WPU-Ag@S-0.50 at room temperature for different times.

Self-healing time	$\sigma_s/\text{MPa}$	$\eta_\sigma/\%$	$\epsilon_s/\%$	$\eta_\epsilon/\%$
10 min	1.17	92.13	585.41	62.62
20 min	1.22	96.06	772.32	82.62
30 min	1.25	98.69	1141.30	122.09
Original	1.27	—	934.82	—