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Supporting Online Materials

UV-Induced Self-Repairing Polydimethylsiloxane-Polyurethane (PDMS-PUR) Cu-

Catalyzed Networks

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Figure S1. NMR spectra of PDMS

In order to determine the number of repeated units in PDMS, ¹H NMR spectra shown in Figure S1 were recoreded. The area ratios for ^aH and ^bH resonances was determined to be 4 : 61.72. The average molecular weight of PDMS was determined by ratioing a:b=4:61.72 and number of repeating units n=61.72÷6=10.3, giving $M_n = 877.2$.



Figure S2. NMR spectra of HDI

In order to determine the composition of the isocyanate, ¹H NMR spectrum was recorded shown in Figure S2. The area ratio of ^aH : ^bH : ^cH : ^dH = 2 : 2.75 : 2.75 : 1, indicating a 2:3 ratio of mono-HDI and tri-HDI in the composition with no presence of di-HDI.



Figure S3 ATR-IR spectra of: a - $CuCl_2$, b - PDMS, c - HDI, and d - PDMS-PUR-Cu Cl_2 networks.

Figure S3 illustrates ATR-IR spectra of CuCl₂ (a), PDMS (b), HDI (c) and PDMS-PUR-CuCl₂ networks (d). The bands at 1022 and 1080 cm⁻¹ due to asymmetric Si-O stretching and 1250 cm⁻¹ attributed to C-H symmetric deformations of Si-CH₃ group appear in trace b and c, demonstrating that PDMS is copolymerized into PDMS-PUR-CuCl₂ networks. The asymmetric stretching vibration at 2268 cm⁻¹ and symmetric stretching vibration at 1355 cm⁻¹ due to -N=C=O functionalities disappear in trace d, signifying all NCO groups have been reacted. These observations confirms that PUR-PDMS-CuCl₂ networks were successfully synthesized.



Figure S4 Raman spectra of: a - CuCl₂, b- CuCl₂ film deposited form DMF, c - PDMS-PUR-CuCl₂, and d - PEG-PUR-CuCl₂ networks.

Figure S4 illustrates Raman spectra of CuCl₂ (a), CuCl₂ layers deposited form DMF (b), PDMS-PUR-CuCl₂ (c) and PEG-PUR-CuCl₂ networks (d). The band at 285 cm⁻¹ attributed to longitudinal vibrations of Cu-Cl bonds shifts to lower energy, thus suggesting the CuCl₂ oligomers formation. The band at 193 cm⁻¹ due to the transverse vibrations of Cu-Cl bonds is detected in the PDMS-PUR-CuCl₂ network (c), while the band at 285 cm⁻¹ diminishes to minimum, manifesting the formation of Cu-O coordination bond. Figure S5 A illustrates the formation of CuCl₂ oligomers, and Figure S5 B shows transverse and longitudinal vibrational modes of Cu-Cl bonds detected in Raman measurements.



Figure S5 A - Schemetic representation of two structure of copper chloride. B - Transverse and longitudinal vibrational modes of Cu-Cl bonds.



Figure S6 ATR-IR spectra of: a - PEG-PUR-DBTDL, b - PDMS-PUR-DBTDL, c - PEG-PUR-CuCl₂, and d - PDMS-PUR-CuCl₂ networks.

Figure S6 illustrate ATR-IR spectra of PEG-PUR-DBTDL (a), PDMS-PUR-DBTDL (b), PEG-PUR-CuCl₂ (c) and PDMS-PUR-CuCl₂ (d) networks. The bands at 1097 and 1093 cm⁻¹ due to asymmetric vibrations of C-O-C entities in PEG are detected in Traces a and c, demonstrating PEG macromonomer incorpration into PEG-PUR network . The bands at 1080 cm⁻¹ and 1022 cm⁻¹ due to asymmetric vibrations of Si-O-Si in PDMS observed in Traces b and d demonstrate that PDMS was incorprated into PDMS-PUR network.



Figure S7. Raman spectra of PDMS-PUR networks in the 120-580, 620-670 and 2800-3500 cm⁻¹ regions collected from of undamaged (A1-A3) and damaged (B1-B3) areas as a function of UV exposure for 0 h (a), 0.5 h (b), and 2 h (c).

Figure S8. Raman spectra of PEG-PUR networks in the 200-600, 900-1200, and 1600-1900 cm⁻¹ regions collected from undamaged (A1-A3) and damaged (B1-B3) areas as a function of UV exposure for 0 (a), 0.5 (b), and 2 hrs (c).