

Mechanical Strong, Highly Adhesive, Recyclable and Transparent Supramolecular Silicone Coatings with Easy Water/Oil Sliding

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 Electronic Supplementary Information

Abstract Traditional silicone materials have poor mechanical properties, poor interfacial adhesion and lack the ability to be reprocessed or recycled. Herein, we developed a novel strategy of incorporating dynamic noncovalent bonds (2-amino-4-hydroxy-6-methylpyrimidine (UPy)) into side chain of silicone backbones to construct supramolecular silicone poly(urea-urethane) (SSPu) coatings with excellent mechanical performance, strong interfacial adhesion and multiple time recycling capability. Impressively, the prepared SSPu is endowed with simultaneously enhanced stiffness (272.0 ± 23.2 MPa) and toughness (8.0 ± 2.0 MJ·m⁻³). Besides, SSPu shows strong interfacial adhesion (up to 9.0 ± 1.3 MPa) to diverse substrate (stainless steel, aluminum, copper, epoxy and glass) with long term stability. Moreover, SSPu exhibits excellent multi-recyclability and reusability without significantly decrease of its performance. In addition to the abovementioned features, the enrichment of siloxane backbones in the surface layer endows SSPu with robust repellency to water/oil. Our strategy provides a powerful route to fabricate a new multifunctional silicone elastomer. It is highly anticipated that our strategy can effectively extend the service life of silicone coating which can be applied in a wide variety of areas including self-cleaning, antifouling.

Keywords Silicong coating; Supramolecular; Adhesion; Recyclable

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INTRODUCTION

As the fastest developing branch of element organic polymer, silicone elastomers have been widely used in daily life and industry due to the exceptional physicochemical and mechanical properties including high flexibility and transparency, waterproof properties, great thermal and chemical resistance, excellent dielectric properties and biocompatibility.^[1,2] Nevertheless, traditional silicone materials have poor mechanical properties, poor interfacial adhesion and cannot be recycled.^[3,4] With the rapid progress of emerging technologies requiring high-performance polymeric materials, it is imperative to develop a new sustainable silicone material with high mechanical strength, high interfacial bonding and recyclability. Through the application of intermediate paint,^[5] the introduction of inorganic fillers^[6] (SiO₂, CaCO₃, TiO₂, graphene oxide (GO), carbon fibre, etc.), acrylic resin,^[7] polyurea/urethane,^[8–10] epoxy resin segments,^[11,12] catechol

groups,^[13,14] the mechanical strength and the substrate adhesion of the silicones can be improved to a certain extent. By introducing coordination bond,^[15–18] boron oxygen unit,^[19,20] hydrogen bond,^[20–22] imine bonds,^[23–26] disulfide bond^[27,28] or other dynamic groups,^[29–33] the silicone material can be endowed with the performance of recycling. However, the above modification methods may have a certain impact on the inherent excellent properties (e.g., transparency and waterproof properties) of silicone. In addition, the synergistic improvement of mechanical properties, substrate adhesion and recycling cannot be achieved simultaneously so far. Therefore, it is still a great challenge to synchronously endow silicone materials with high strength, high substrate adhesion and recyclability without affecting its excellent performance.

Herein, we report a novel supramolecular silicone poly(urea-urethane) (SSPu) coatings with excellent mechanical performance, strong interfacial adhesion and multiple time recycling capability. SSPu is prepared based on the strategy of incorporating noncovalent bonds (2-amino-4-hydroxy-6-methylpyrimidine (UPy))^[34–37] quadruple hydrogen bonds) into the side chain of silicone backbone (Fig. 1). The UPy functionalized siloxane oligomers could self-assemble into supramolecular^[38–41] silicone attributed to the high association en-

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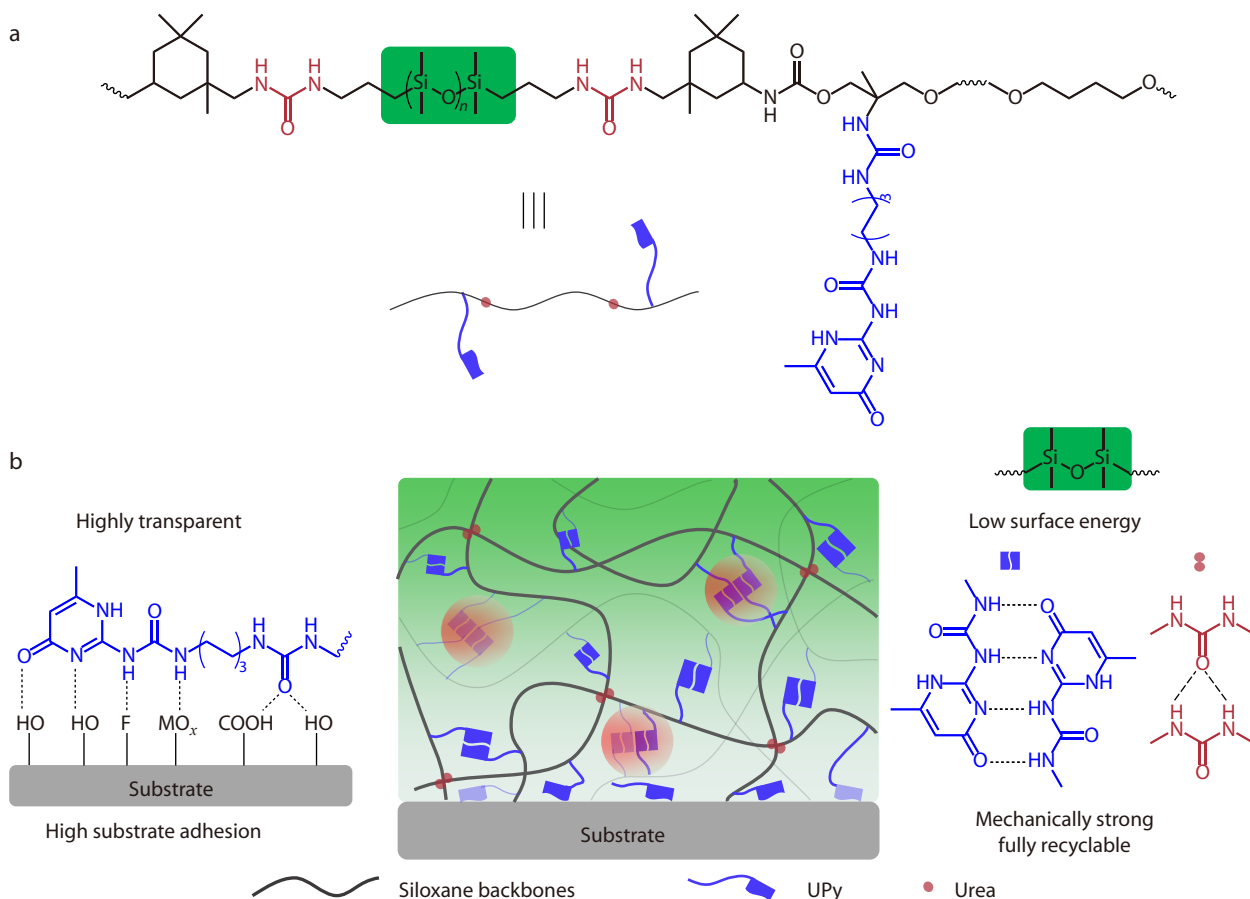


Fig. 1 (a) Chemical structure of siloxane oligomer with 2-amino-4-hydroxy-6-methylpyrimidine (UPy) motif at the side chain; (b) Structure of the transparent SSPu coating on a substrate. The siloxane backbone enriched in the surface of the SSPu coating offer the properties of low surface energy; the multiple hydrogen bonds in the interior of the SSPu coating make it with enhanced mechanical properties and fully recyclable. The strong interaction between the SSPu coating and the substrate through hydrogen bonding enables the coating to firmly adhere to various substrates.

ergy of UPy dimers. The complementary hydrogen bonding provided by the UPy motifs endows SSPu with enhanced mechanical properties (simultaneously enhanced toughness (272.0 ± 23.2 MPa) and stiffness (8.0 ± 2.0 MJ·m⁻³)). Besides, owing to the high-density UPy motifs enriched at the coating/substrate boundary, SSPu shows strong interfacial adhesion (up to 9.0 ± 1.3 MPa) to diverse substrate. Moreover, benefiting from the dynamic and reversible property of quadruple hydrogen bonds, SSPu exhibits excellent multi-recyclability and reusability without significantly decrease of its performance. In addition to the abovementioned features, the enrichment of siloxane backbones in the surface layer enables SSPu with robust repellency to water/oil.

EXPERIMENTAL

Materials

Chemicals were purchased from commercial sources and used as received, unless otherwise stated. 2-amino-4-hydroxy-6-methylpyrimidine, 2-amino-2-methyl-1,3-propanediol (AMPD), hexamethylene diisocyanate (HDI) and 2-methyl-1,3-propanediol (MPO) were purchased from Aladdin Biochemical Technology Co., Ltd. *n*-Hexane, acetone, chloroform, *N,N*-

dimethylformamide (DMF) and ethyl ether were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Isophorone diisocyanate (IPDI), 1,4-butanediol (BDO) and ditin butyl dilaurate (DBTDL) were purchased from Macklin Biochemical Co., Ltd., Shanghai, China. Anhydrous pyridine was purchased from Adamas Reagent Co., Ltd., Shanghai, China. Polydimethylsiloxane (PDMS, SYLGARD™ 184 Silicone Elastomer Kit) was purchased from Dow Corning. Poly(dimethylsiloxane) bis(3-aminopropyl) terminated ($\text{H}_2\text{N-PDMS-NH}_2$, $M_w \sim 1000$ g/mol, 2000 g/mol, 3000 g/mol) was purchased from Hangzhou Silong Material Technology, China. AMPD was heated in a vacuum oven at 60 °C overnight before use. HDI, MPO, chloroform and DMF were dehydrated with 4 Å molecular sieve before use.

Synthesis of 2-(6-Isocyanato-hexylamino)-6-methyl-4[1H]-pyrimidone (UPy-NCO)

The synthesis of UPy-NCO was performed according to literature previously published.^[42] In detail, 2-amino-4-hydroxy-6-methylpyrimidine (80 mmol, 10.3 g) was mixed with 6 equiv. of HDI (480 mmol, 81.5 g). The mixture was stirred at 90 °C for 24 h under N_2 environment. The reaction mixture was extensively washed by hexane to remove the unreacted HDI. The product was dried at 60 °C under vacuum overnight to obtain white

powder (23.1 g, yield, 98%). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , ppm) 13.14 (s, 1H), 11.89 (s, 1H), 10.23 (t, 1H), 5.84 (s, 1H), 3.29–3.26 (m, 4H), 2.25 (s, 3H), 1.68–1.60 (m, 8H).

Synthesis of U2-diol (UD) Molecule

The synthesis of UD was performed according to a literature with some modification.^[42] UPy-NCO (44.2 mmol, 13.2 g) was mixed with AMPD (60.9 mmol, 6.4 g) in dried CH_3Cl solution. The mixture was stirred at 60 °C for 6 h under N_2 atmosphere. After reaction, the product was filtrated and washed by CH_3Cl and then DI water. After that, the white product was collected by centrifugation. The product was dried at 60 °C under vacuum to obtain light yellow powder (14.1 g, yield, 80%). $^1\text{H-NMR}$ (400 MHz, DMSO, δ , ppm) 9.92 (s, 2H), 8.28 (s, 1H), 6.18 (t, 1H), 5.65 (s, 1H), 5.12 (s, 2H), 3.37–3.3 (m, 4H), 3.14 (d, 2H), 2.94 (d, 2H), 2.11 (s, 3H), 1.46–1.24 (m, 8H), 1.08–1.05 (m, 3H).

Synthesis of SSPu Elastomer with Different Molecular Weight and UPy Molar Ratio (PxUy)

The polymers are denoted as PxUy, where P and U represent poly(dimethylsiloxane) segment and U2-diol, respectively, x means the molecular weight of $\text{H}_2\text{N-PDMS-NH}_2$ and y means the molar percentage of U2-diol molecule of all the chain extender. The synthesis procedure of P1000U40 was described as follows: $\text{H}_2\text{N-PDMS-NH}_2$ (10 mmol, 10 g) was stirred under vacuum at 120 °C for 2 h to remove moisture residue and then cooled to 80 °C. IPDI (19 mmol, 4.23 g) dissolved in 5 mL of anhydrous DMF and DBTDL (32 μL) was added and stirred for 2 h under N_2 atmosphere. Moreover, U2-diol (3.2 mmol, 0.43 g) in anhydrous DMF (5 mL) was added and stirred until it was dissolved totally. After that, BDO (4.8 mmol, 0.43 g) in anhydrous DMF and DBTDL (32 μL) were added into the mixture and further stirred for 2 h at 80 °C. The product was then dissolved with CH_3Cl (50 mL) and washed with DI water (50 °C, 50 mL). The solution was poured into a Teflon mold at room temperature to evaporate the solvent and then dried in a vacuum oven at 70 °C for 72 h to obtain the final product (14.9 g, yield, 93.5%). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , ppm) 13.14 (s, 1H), 11.82 (s, 1H), 9.97 (s, 1H), 5.85 (s, 1H), 3.97–3.48 (m, 10H), 3.15 (s, 11H), 2.27 (s, 3H), 1.51 (s, 13H), 1.06 (s, 30H), 0.99–0.78 (m, 36H), 0.09 (s, 197H).

Synthesis of Silicone Polymers without UPy Motif (P1000M)

The synthesis procedure of P1000M is similar to that of PxUy, except for using MPO instead of U2-diol as the chain extender.

Preparation of PxUy Films

The as-prepared P1000U10 powder (1 g) was dissolved in CH_3Cl (20 mL) and then casted onto the glass slide. A homogenous film was obtained after the slowly evaporation of the solvent. Self-standing samples were prepared by transferring the solution into a Teflon mould and then detached from the Teflon surface.

Characterization

Fourier transform infrared (FTIR) Spectra were collected on a Nicolet 5700 FTIR spectrometer (Thermo Fisher, U.S.A.) equipped with a diamond attenuated total reflectance (ATR) window. $^1\text{H-NMR}$ spectra was recorded on a Bruker 400 MHz NMR spectrometer (Bruker, Germany) using CDCl_3 and d-DMSO as the solvent. Molecular weights (M_n and M_w) and polydispersity (PDI) were determined by Agilent PL-GPC220 gel

permeation chromatography (GPC) instrument with THF as mobile phases at a flow rate of 4 mg/mL. X-ray photoelectron spectroscopy (XPS) was performed on a VG MultiLab 2000 XPS spectrometer (Thermo Electron, U.S.A.). All the binding energies were calibrated by C 1s peak at 284.8 eV. Thermal gravimetric analysis (TGA) was performed on the METTLER TGA/SDTA 851 instrument. Samples (about 5–10 mg) were heated from 30 °C to 800 °C at the heating rate of 10 °C/min in nitrogen atmosphere. 2D Small angle X-ray scattering (SAXS) studies on polymer films were carried out on a SAXS instrument (NanoSTAR U, Bruker) equipped with a microfocus X-ray source operating at $\lambda=0.154$ nm. The water contact angle (WCA) was determined by a drop shape analyser DSA 25 instrument (Kruss, Germany) using a 4 μL of DI water droplet at ambient temperature, and each sample was measured for three times to obtain the average value with standard deviations. The droplet adhesion force was measured by a force tensiometer K100MK2 instrument (Kruss, Germany) using a 4 μL of DI water droplet at an immersion depth of 0.1 mm and immersion time of 0.01 min at ambient temperature, and each sample was measured for five times to obtain the average value and standard deviations. Scanning electron microscopy (SEM) images were obtained using a field emission scanning electron microscopy (JSM-7500F, JEOL, Japan). Lap shear strength testing was carried out using a procedure described in ASTM D1002-10 on a universal materials tester equipped with a 5 kN load cell with a rate of shear of 0.5% per minute. The bonded overlap area was 12.7 mm $\times$ 10 mm. Adhesion strength was determined by the maximum load divided by the bonded overlap area. Failure mode was assessed visually. Five samples were measured to obtain an average lap shear strength.

RESULTS AND DISCUSSION

Preparation and Characterizations of SSPu Elastomers

The preparation procedure of SSPu is illustrated in Scheme S1 (in the electronic supplementary information, ESI). According to the literature previously published,^[42] we first prepared UPy-NCO as precursor using 2-amino-4-hydroxy-6-methylpyrimidine and hexamethylene diisocyanate (HDI). The structure of UPy-NCO was confirmed by $^1\text{H-NMR}$ in Fig. S1(A) (in ESI). Then U2-diol (UD) molecule was prepared by UPy-NCO and 2-amino-2-methyl-1,3-propanediol (AMPD). The $^1\text{H-NMR}$ (Fig. S1B in ESI) and FTIR results (Fig. S1C in ESI) confirmed the chemical structure of the new diol molecular structure with the urea/urethane and UPy segments. SSPu was prepared through polycondensation of poly(dimethylsiloxane) bis(3-aminopropyl) terminated ($\text{H}_2\text{N-PDMS-NH}_2$), isophorone diisocyanate (IPDI), UD and 1,4-butanediol (BDO, another diol molecule). A series of SSPu (Table S1 in ESI), denoted as PxUy, were synthesized, where x ($x=1000, 2000$ and 3000) represented the molecular weight of $\text{H}_2\text{N-PDMS-NH}_2$ and y ($y=5, 10, 20, 30$ and 40) represented the molar ratio ($x\%$) of UD in the diol (UD and BDO). SSPu without UPy motif (P1000M) was also synthesized without UD for comparison. The result SSPu films manifested good transparency at different UPy concentration (Fig. S2 in ESI).

Gel permeation chromatography (GPC) measurement shows that the SSPu elastomers (P1000Uy) possess high molecular weight varying from 7275 to 11340 (Table S2 in ESI).

The chemical structures of SSPu elastomers were investigated by ^1H -NMR and FTIR spectroscopy. As shown in Fig. S3(A) (in ESI), three typical characteristic peaks (13.14, 11.82 and 9.97 ppm) assigned to UPy motif in the ^1H -NMR spectra of SSPu (P1000U40) demonstrate the successfully incorporation of UPy motif into silicone elastomer. With same x ($x=1000$), the typical characteristic peaks (9–14 ppm) assigned to UPy motif in the ^1H -NMR spectra increase as y increases (Fig. S3B in ESI). With the same y ($y=10$), the typical characteristic peaks (9–14 ppm) assigned to UPy motif in the ^1H -NMR spectra decrease as x increases (Fig. S3C). The FTIR spectra of SSPu elastomers are shown in Figs. S3(D)–S3(F). No band assigned to $-\text{NCO}$ appears. Bands at 3326 and 1566 cm^{-1} correspond to the stretching vibration and bending vibration of $-\text{NH}$ group, respectively. Bands at 1704 and 1626–1665 cm^{-1} are typical $\text{C}=\text{O}$ stretching vibration bands. Among them, band at 1704 cm^{-1} corresponds to the $\text{C}=\text{O}$ stretching vibration of carbamate. Bands at 1626 and 1651 cm^{-1} correspond to the disordered and ordered $\text{C}=\text{O}$ stretching vibration of urea/urethane group. Band at 1665 cm^{-1} corresponds to the $\text{C}=\text{O}$ stretching vibration of UPy group. With the increase of UD molecular content (y), the hydrogen bond concentration in the elastomer increases rapidly, causing the averaging of the electron cloud. The infrared absorption bands shift to the low wavenumber (Fig. S3B in ESI). All these results demonstrate that SSPu elastomers were successfully synthesized.

Due to the unique molecular structure, SSPu elastomers

show self-stratifying effect. The surface layer and the bottom layer of SSPu elastomer were tested relatively for comparison by attenuated total reflectance infrared (ATR-IR) and X-ray photoelectron spectroscopy (XPS). Higher relative intensity of the peak assigned to siloxane groups in the surface layer is observed in ATR-IR (Fig. S4 and Table S3 in ESI), implying that the siloxane motifs are enriched in the surface layer of the coatings. In contrast, higher relative intensity of peak assigned to $-\text{C}=\text{O}$ and $-\text{NH}$ groups in the bottom layer are observed, demonstrating that the polar groups (UPy, urethane and urea) are enriched in the bottom surface at the coating/substrate interface. Similar results can be observed in XPS spectra (Figs. S5–S11 and Table S4 in ESI). Higher silicon atom content in the surface layer and higher nitrogen atom content in the bottom layer of each sample are observed.

Mechanical Properties

The mechanical properties of SSPu elastomers, as well as P1000M and neat PDMS (Dow corning 184 git), were investigated by tensile test according to ISO 37:2005. As shown in Figs. 2(a)–2(d) and Table S5 (in ESI), neither PDMS nor P2000U10 and P3000U10 show yield phenomenon while P1000M and P1000Uy show simultaneous high stiffness and toughness. This indicates that the mechanical properties of silicone elastomer can be effectively enhanced by the introduction of strong, reversible, and sacrificial multiple hydrogen bonds (urea/urethane hydrogen bonds and UPy quadruple hydrogen bonds) which offers stronger interchain

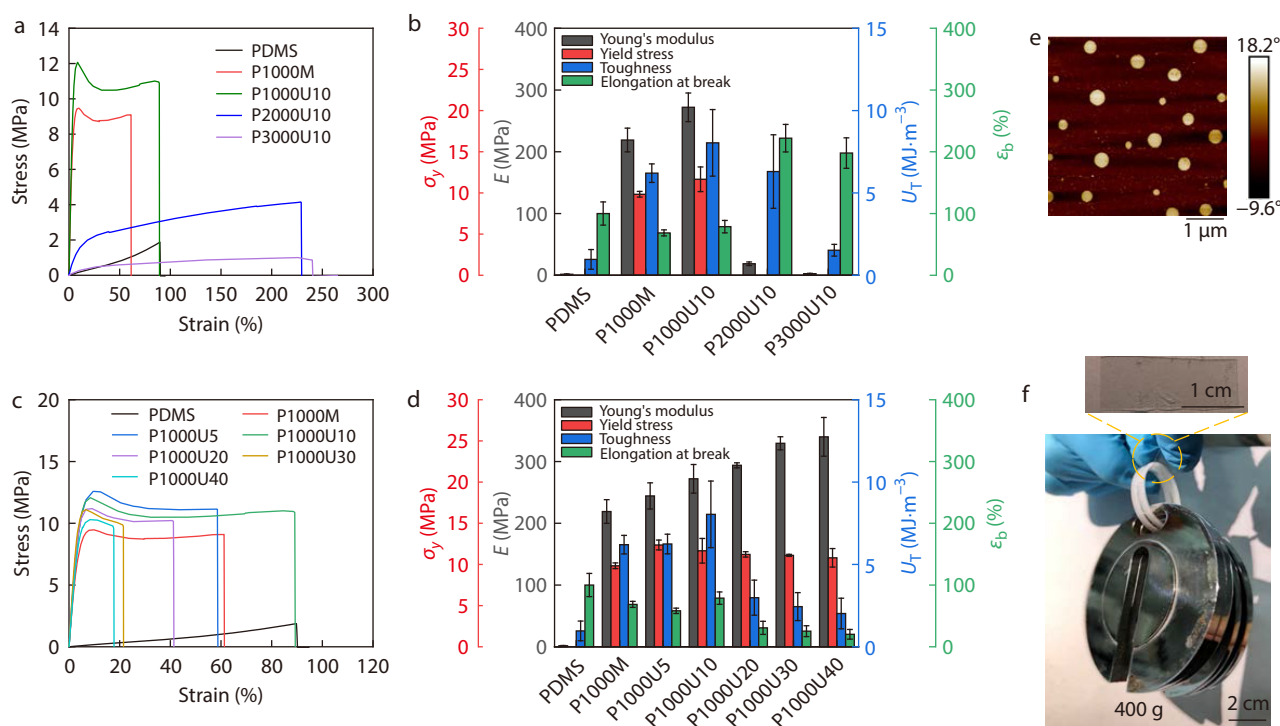


Fig. 2 Characterization of the mechanical properties of the SSPu elastomer. (a) Typical strain-stress curves of the PDMS, P1000M and SSPu (P1000U10, P2000U10 and P3000U10); (b) Comparison of the Young's modulus, yield stress, toughness and elongation at break of the PDMS, P1000M, P1000U10, P2000U10 and P3000U10; (c) Typical strain-stress curves of the PDMS, P1000M and SSPu (P1000U5, P1000U10, P1000U20, P1000U30 and P1000U40); (d) Comparison of the Young's modulus, yield stress, toughness and elongation at break of the PDMS, P1000M, P1000U5, P1000U10, P1000U20, P1000U30 and P1000U40; (e) AFM phase image of P1000U10. Scale bar=1 μm . (f) Digital images of P1000U10 film (thickness: 0.1 mm) to lift an object with weight of 400 g.

interactions and increases energy dissipation. With the increase of the length of siloxane backbones, the enhancement of hydrogen bonds decreases. Compared with P1000M, the Young's modulus and toughness of P1000U10 increase by ~23% and ~33%, respectively. It indicates that the introduction of UPy quadruple hydrogen bonds plays a key role in improving the mechanical properties of silicone elastomer. Due to the self-assembly effect of UPy quadruple hydrogen bond, the P1000Uy elastomers show semi-crystalline property which is confirmed by XRD (Fig. S12 in ESI). In addition, the increasing of H-bonds can also induce microphase separation, which is confirmed by AFM phase images (Fig. 2e and Fig. S13 in ESI) and SAXS images (Fig. S14 in ESI). With increase of UPy motif, the mechanical properties of the SSPu are gradually enhanced. Unfortunately, excessive phase separation will also deteriorate the mechanical properties of the polymer. Remarkably, the prepared P1000U10 presents the best mechanical property with Young's modulus of 272.0 ± 23.2 MPa (170 times greater than that of PDMS) combined with a toughness of 8.0 ± 2.0 MJ·m⁻³ (7 times greater than that of PDMS). An object (400 g) can be easily lifted using P1000U10 film with thickness of only 0.1 mm (Fig. 2f).

Adhesive Properties

The adhesive strengths of SSPu elastomers, as well as pure PDMS (Dow corning 184 git) and P1000M, were investigated in single-lap shear on stainless steel (SUS) according to ASTM D1002-10. The testing samples are prepared according to the literature.^[35] The adhesive strengths were measured by shear testing at room temperature and the failure modes were

determined by visual inspection of fractured lap joints (Fig. 3a and Fig. S15 in ESI). Neat PDMS exhibited a low adhesive strength of 0.6 ± 0.2 MPa (adhesive failure). For the P1000M, a remarkable increase (3.8 ± 0.9 MPa, adhesive failure) in adhesive strength compared to PDMS was achieved, indicating that the introduction of urea/urethane hydrogen bond can effectively enhance the adhesive property. The introduction of UPy quadruple hydrogen bonds can further enhance the adhesion of polymers. With the increase of UPy motif, the adhesive strength increases from 4.2 ± 1.1 MPa (P1000U5, mix failure) to 5.6 ± 1.1 MPa (P1000U10, mix failure). It is worth noting that the adhesion failure mode changes from adhesive failure to mixed failure after the introduction of UPy, which indicates that UPy quadruple hydrogen bond can reinforce the interfacial strength between polymer and substrate more effectively compared with urea/urethane hydrogen bond. However, with the further increase of UPy motif, the adhesion began to decrease due to the decline of the mechanical property of the adhesive itself (cohesion). The adhesive strengths of P1000U20, P1000U30 and P1000U40 are 3.9 ± 0.8 MPa (mix failure), 3.2 ± 0.3 MPa (mix failure) and 2.5 ± 0.7 MPa (mix failure), respectively. Besides, the adhesive strength of SSPu is influenced by the molecular weight of siloxane backbone. The adhesive strengths of P1000U10, P2000U10 and P3000U10 (Fig. 3b and Fig. S16 in ESI) decrease from 5.6 ± 1.1 MPa (mix failure) to 4.3 ± 0.5 (mix failure) and then 1.8 ± 0.2 MPa (adhesive failure). Moreover, SSPu also displayed outstanding adhesion strength on various substrates (stainless steel (SUS), aluminium (Al), copper (Cu), epoxy (EP) and glass). As shown in Fig. 3(c) and Fig. S17 (in ESI), the adhesion strengths of P1000U10 to various substrates (stainless steel (SUS), aluminium

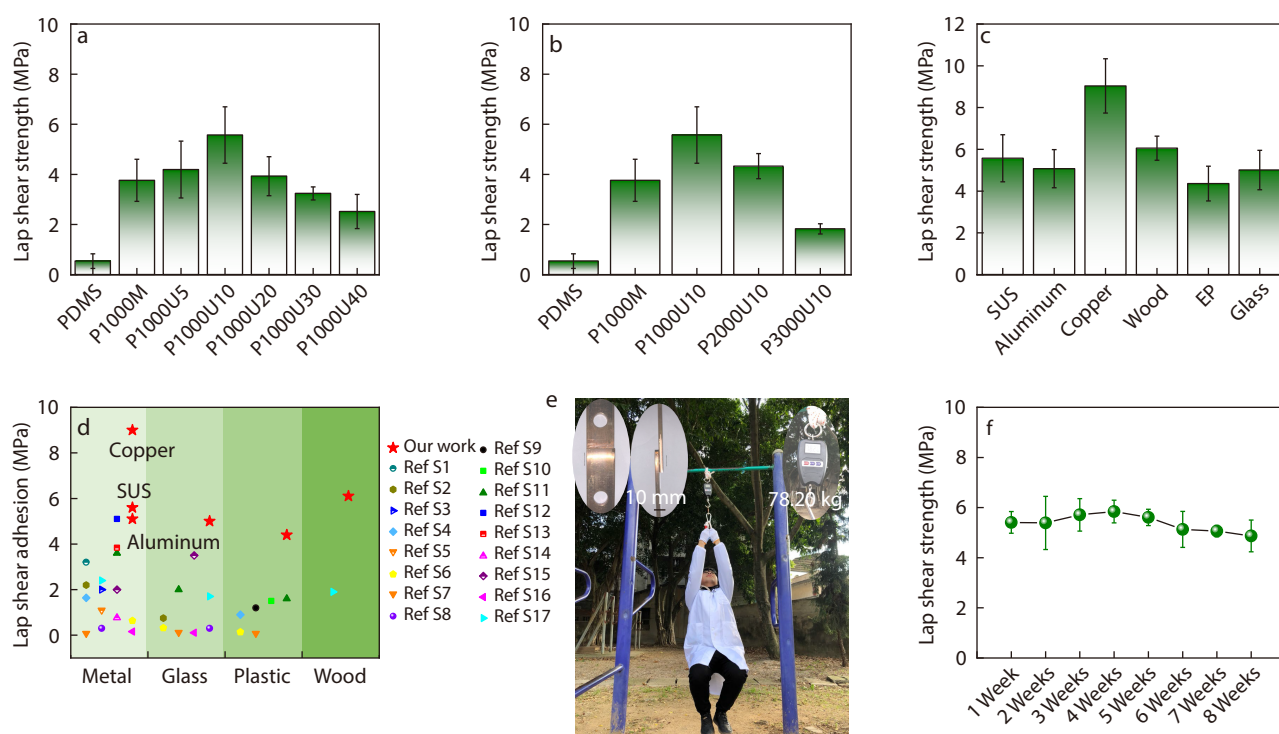


Fig. 3 Adhesion strength of the SSPu elastomer. (a) Lap shear strength of PDMS, P1000M and P1000Uy in bonding stainless steel; (b) Lap shear strength of PDMS, P1000M and PxU10 in bonding stainless steel; (c) Comparison of lap shear strength of P1000U10 on various substates; (d) Adhesion strength of P1000U10 compared to other silicone elastomers reported in the literatures; (e) Digital images of P1000U10 bonding copper of lift an adult (78.20 kg) with a bonding area of 12.7 mm × 10 mm; (f) Adhesive strength of P1000U10 versus time.

(Al), copper (Cu), epoxy (EP) and glass) are significantly larger than that of PDMS. Particularly, P1000U10 shows a maximum adhesive strength to Cu of 9.0 ± 1.3 MPa and a minimum adhesive strength to EP of 4.4 ± 0.3 MPa. We compared the adhesion strength on different surfaces against literature reports (Table S6 in ESI) and found that P1000U10 had superior adhesion strengths on every surface (Fig. 3d and Table S6 in ESI). P1000U10 adhesive ($1.5 \text{ cm} \times 1.5 \text{ cm}$) bonded copper sheet can easily lift an adult ($\sim 78 \text{ kg}$) without breaking (Fig. 3e).

To further evaluate the adhesion of SSPu adhesive, long-term stability test was conducted. P1000U10 adhesives were placed at room temperature for different time (0–56 days) and the adhesive strength was tested every 7 days. Fig. 3(f) and Fig. S18 (in ESI) show that the adhesive strength of P1000U10 remains unchanged. On the other hand, SSPu elastomers show outstanding thermal stability. Thermogravimetric (TG) test shows that its decomposition temperature in air and nitrogen atmosphere is 265 and 282 °C, respectively (Fig. S19 in ESI). We tested the adhesion strength of P1000U10 adhesive after heating for 2 h at different temperatures (100–200 °C). The adhesive strength of P1000U10 still maintain ~ 4 MPa even after heated to 200 °C (Figs. S19A and Figs. S20–S22 in ESI). We also tested the adhesion strength of P1000U10 adhesive after heating at 130 °C for different time

(2, 5, 8 and 10 h). The adhesive strength of P1000U10 still maintain ~ 5.5 MPa after aging for 10 h (Figs. S20B and S23 in ESI). SSPu shows long-term adhesion strength stability which is critical for practical application.

Self-Healing and Recycling Properties

SSPu exhibits excellent self-healing properties (Fig. S24 in ESI). The self-healing properties is influenced by the molecular weight of siloxane backbone and self-healing temperature. Another key characteristic of SSPu is their recyclability while sustaining material properties. To show the recyclability of SSPu elastomers, we performed two reprocessing processes, solution treatment and hot compression cycles (Fig. 4a). The P1000U10 elastomer was used as the example. The sample could be dissolved in chloroform or ethanol, demonstrating its noncovalent crosslinking. After solvent evaporation and heating under vacuum, the homogeneous elastomer was regenerated. The retention of highly transparency was confirmed by the UV-Vis-NIR spectroscopy, which yielded transmittance similar to that of pristine SSPu (Fig. 4b and Fig. S25 in ESI). The tensile results show that the recycled elastomer can recuperate most of their initial mechanical properties (Fig. 4c and Table S7 in ESI). For example, the recovery ratio of Young's modulus and toughness are 96.3% and 86.3%, respectively. Notably, after being recycled for 10 times, SSPu (P1000U10) still exhibits nice

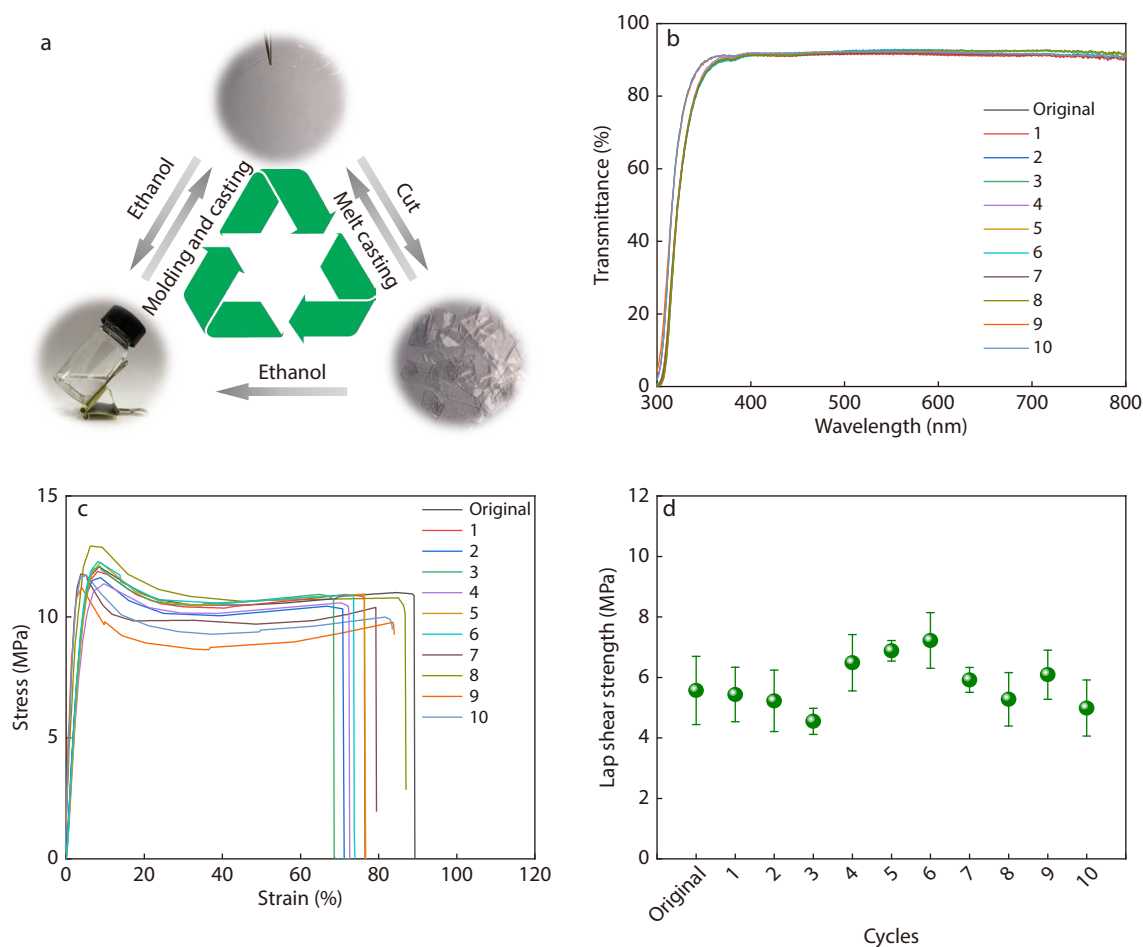


Fig. 4 Recycling properties of SSPu. (a) Scheme of recycling route (solution treatment and hot compression cycles) of SSPu; Comparison of transparency (b), mechanical properties (c) and adhesion strength (d) of the SSPu before and after recycling.

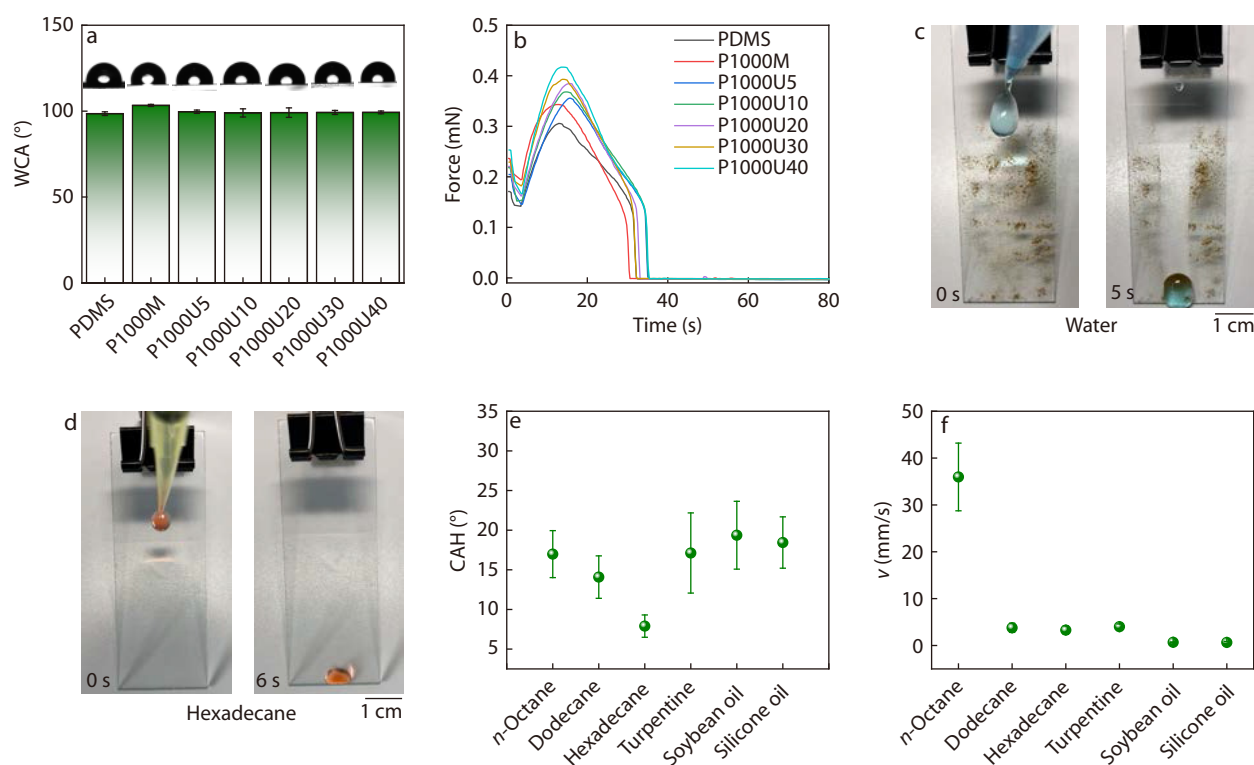


Fig. 5 Wettability of the SSPu coatings. (a) Comparison of water contact angle of PDMS, P1000M and P1000Uy; (b) Droplet adhesion of the SSPu coatings; (c) Self-cleaning of glass slide coated with P1000U10; (d) Easy oil sliding on P1000U10; (e) CAHs of various liquids on glass slides coated with P1000U10; (f) Sliding velocity of various liquids.

elasticity with a Young's modulus of 209.8 ± 24.6 MPa and a toughness of 8.2 ± 0.6 MJ·m⁻³. The good recyclable nature was also evidenced by the hot compression cycles. The sample was cut into pieces and then remoulded at 130 °C under 10 MPa for 2 h. The recycled sample is still adhesive, which remains stable with the adhesive strength of around 5 MPa to 6 MPa even after 10 cycles (Fig. 4d and Figs. S26 and S27 in ESI). All these experiments demonstrate the excellent recyclability of SSPu elastomer.

Oil/Water Sliding

Many of the applications of the silicone polymer are a consequence of its low surface tension and hydrophobic nature. One of the preconditions for the modification of silicone polymers is that these excellent properties cannot be affected. Owing to the high-density siloxane backbones enriched at the surface, all SSPu elastomers exhibit low surface energy similar to traditional silicone (PDMS). Surface wettability was used to evaluate the surface energy of the SSPu. As shown in Fig. 5(a), the introduction of UPy motif has little effect on the WCAs. Besides the static contact angle, the dynamic behavior (droplet adhesion) of the droplet on the SSPu are conducted. As shown in Fig. 5(b), the droplet adhesion forces of all SSPu elastomers are similar to that of PDMS. Even smooth SSPu surface (Fig. S28 in ESI) exhibits self-cleaning property (Fig. 5c and Videos S1 and S2 in ESI). In further evaluation, we also tested the oil repellency of SSPu. Nonpolar organic solvent, including *n*-hexane, *n*-dodecane, *n*-hexadecane, and commercial edible oils (e.g., turpentine, soybean oil and silicone oil) were taken as probe liquids. As shown in Fig. 5(d) and Video S3 (in ESI), 20 μL of *n*-

hexane drops can slide easily. All the probe liquids exhibit contact angle hysteresis (CAH) lower than 15°, indicating the easy sliding/dewetting of the SSPu coatings (Figs. 5e and 5f). The ease of oil dewetting on SSPu coatings could be ascribed to the weak interaction between the oil droplet and the siloxane-enriched surface where the UPy motifs on the surface layer are shielded by the siloxane motifs.

CONCLUSIONS

In this study, we developed a novel supramolecular silicone poly(urea-urethane) (SSPu) coatings with excellent mechanical performance, strong interfacial adhesion and multiple time recycling capability. SSPu is prepared based on the strategy of incorporating UPy quadruple hydrogen bonds into silicone main chains. The UPy functionalized siloxane oligomers could self-assemble into supramolecular silicone.

The complementary hydrogen provided by the UPy motifs endows SSPu with enhanced mechanical properties (simultaneously enhanced toughness and stiffness). Optimized SSPu can present mechanical property with Young's modulus of 272.0 ± 23.2 MPa (170 times greater than that of PDMS) combined with a toughness of 8.0 ± 2.0 MJ·m⁻³ (7 times greater than that of PDMS). Besides, owing to the high-density UPy motifs enriched at the coating/substrate boundary, SSPu shows strong interfacial adhesion (up to 9.0 ± 1.3 MPa) to diverse substrate (stainless steel, aluminum, copper, epoxy and glass) with long term stability. Moreover, benefiting from the dynamic and reversible property of UPy quadruple hydrogen bonds, SSPu exhibits excellent multi-recyc-

lability and reusability without significantly decrease of its performance. In addition to the abovementioned features, the enrichment of siloxane backbones in the surface layer enables SSPu with robust repellency to water/oil. Our strategy provides a powerful route to fabricate a new multifunctional silicone elastomer. We envision that our strategy can effectively extend the service life of silicone coating which can be applied in a wide variety of areas including self-cleaning, anti-fouling.

Conflict of Interests

The authors declare no interest conflict.



Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-023-2966-7>.

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