

Poly(hydroxy urethane-siloxane) Pressure-sensitive Adhesive: Synthesis, Characterization and Its Usage for Skin-contact Sensors

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Electronic Supplementary Information

Abstract Silicone-based pressure-sensitive adhesives (Si-PSAs) are valued for their thermal stability, flexibility, and biocompatibility, but their weak bonding strength restricts high-performance use. Polyurethane-modified Si-PSAs enhance adhesion, however diisocyanates remain essential. The raw materials of isocyanates are toxic, and their synthesis involves phosgene. To make up for those shortcomings, a series of poly(hydroxy urethane-siloxane) PSAs, named as PHUSi here, were synthesized through the ring-opening reaction of cyclic carbonate-functionalized polysiloxanes (PSi_x-VEC₂) with various aliphatic diamines. The PSi_x-VEC₂ precursors were prepared *via* the hydrosilylation of hydrogen-containing polysiloxanes (PSi_x-H_y) with 4-vinyl-1,3-dioxolan-2-one (VEC). The chemical structures of PSi_x-H_y, PSi_x-VEC₂ and PHUSi were characterized, and bonding properties of PHUSi were systematically evaluated. The influence of architectures on adhesive performance was elucidated through comprehensive analyses, including rheology, crosslink density assessment, and so on. These studies revealed that the tailored design of PHUSi adhesives combine the advantages of traditional Si-PSAs with enhanced adhesion while eliminating isocyanate toxicity. The optimized PHUSi formulation achieved remarkable 180° peel strength (76.5 N/m on skin) and maximum probe tack force (1.61 N), enabling secure 24 h attachment of flexible sensors to skin. These properties make PHUSi particularly suitable for medical applications, as demonstrated by successful implementation in flexible electrocardiogram devices, offering a biocompatible, high-performance adhesive.

Keywords Pressure-sensitive adhesives; Polysiloxane; Polyhydroxyurethane; Cyclic carbonate; Skin-contact sensor

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INTRODUCTION

Pressure-sensitive adhesives (PSAs) for skin-contact applications need to meet unique requirements, including good holding power on the skin, prolonged wear time, and easy and painless removal after use without leaving residues. Silicone-based PSA is renowned for its excellent weather resistance, flexibility, gas permeability, and biocompatibility, making it particularly suitable for medical applications that demand good skin adaptability and environmental tolerance.^[1–6] However, their relatively low bond strengths limit their broader applications.

The adhesive performance of PSAs is governed by van der Waals forces at the PSA-substrate interface and intermolecular interactions within the PSA itself. In polyurethane (PU)-based PSAs, the urethane groups along the polymer back-

bone play a crucial role: (1) they form intramolecular hydrogen bonds, enhancing the cohesive strength and improving the creep resistance by reinforcing the polymer network, and (2) they facilitate intermolecular hydrogen bonding with polar substrates (*e.g.*, skin, medical tapes, or flexible electronics), leading to stronger interfacial adhesion and higher peel strength. This dual contribution makes PU-based PSAs particularly effective for applications that require both durability and reliable bonding^[7]. The PU-modified Si-PSAs retain the advantages of traditional Si-PSAs and exhibit enhanced wear resistance and superior adhesive properties. These properties render them highly suitable for a wide range of emerging applications.^[8–10]

Recently, poly(hydroxy urethane)s (PHU) have emerged as a novel class of PU, which are fabricated by the polyaddition of cyclic carbonates (CC) and amines. PHU are considered as a safer and greener alternative to conventional PU, avoiding the use of toxic phosgene-based isocyanates.^[11–17] PHU contain a high density of polar groups, including urethane linkages on the backbone and hydroxyl groups in the side chain.

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These groups enable the profusion of intramolecular and intermolecular hydrogen bonds, which critically influence the adhesion performance by providing cohesive strength, enhancing substrate interactions, and offering tunable viscoelastic properties. Thus, PHU have promising potential for the development of versatile adhesives.^[12,18–21]

In this study, $\text{PSi}_x\text{-H}_y$ was synthesized by the open-ring reaction of octamethylcyclotetrasiloxane (D_4) and 2,4,6,8-tetramethylcyclotetrasiloxane (D_4H), and $\text{PSi}_x\text{-VEC}_z$ was obtained by hydrosilylation of vinyl ethylene carbonate (VEC) with $\text{PSi}_x\text{-H}_y$. Finally, a series of PHUSi were synthesized through the ring-opening reaction of $\text{PSi}_x\text{-VEC}_z$ with aliphatic diamines (Fig. 1). The effects of the amount of grafted CC (determining the hydroxyl group density), $-\text{NH}_2/\text{CC}$ molar ratio (impacting crosslink density via urethane formation), types of diamines (influencing chain flexibility and hydrogen bonding potential), and MQ resin content on the bonding properties were systematically evaluated. In view of the strong peel strength and adhesion force of PHUSi, its application in fixing a flexible electrocardiogram (ECG) device to the skin was studied.

EXPERIMENTAL

Materials

Octamethylcyclotetrasiloxane (D_4 , 96%), 2,4,6,8-tetramethyl-

clotetrasiloxane (D_4H , 98%), 1,1,3,3-tetramethyldisiloxane (TMDS 98%), hexamethyl disilylamine (HMDS 98%), vinyl ethylene carbonate (VEC), platinum(II) bis(acetylacetonate) ($\text{Pt}(\text{acac})_2$, 98%), trifluoromethanesulfonic acid (TFSA, 98%), isophorondiamine (IPDA, 99%), and 4,4'-diaminodicyclohexyl methane (DDCM, 98%) were all purchased from Macklin Reagent Co., Ltd. Magnesium sulfate (AR), ethanol absolute (AR), and 1,6-hexamethylenediamine (HMDA, 98%) were all purchased from Aladdin Reagent Co., Ltd. Toluene (AR) was purchased from Yantai Yuandong Co., Ltd. The MQ resin was synthesized in the laboratory according to the literature (details are provided in Fig. S1 in the electronic supplementary information, ESI).^[22,23]

Synthesis of $\text{PSi}_x\text{-H}_y$

$\text{PSi}_x\text{-H}_y$ (x and y represent the theoretical number of $-\text{Si}-\text{O}-$ and $-\text{Si}-\text{H}$ units, respectively) was synthesized by ring-opening polymerization of D_4 and D_4H using TMDS as the end-capping reagent and TFSA as the catalyst. A typical reaction of $\text{PSi}_{14}\text{-H}_4$ is as follows: 185.39 g (0.625 mol) D_4 , 30.06 g (0.125 mol) D_4H and 0.3 wt% TFSA were added into a three-neck flask and mixed together by stirring for 15 min. Then, 33.58 g (0.25 mol) of TMDS was added, and the equilibrium reaction was performed at 30 °C for 24 h under a N_2 atmosphere. After that, 2.45 g of HMDS was added to neutralize the residual TFSA, and 2.0 g of MgSO_4 was added to remove H_2O . After filtration, the oligomer was removed via vacuum distillation to obtain an oily product with a

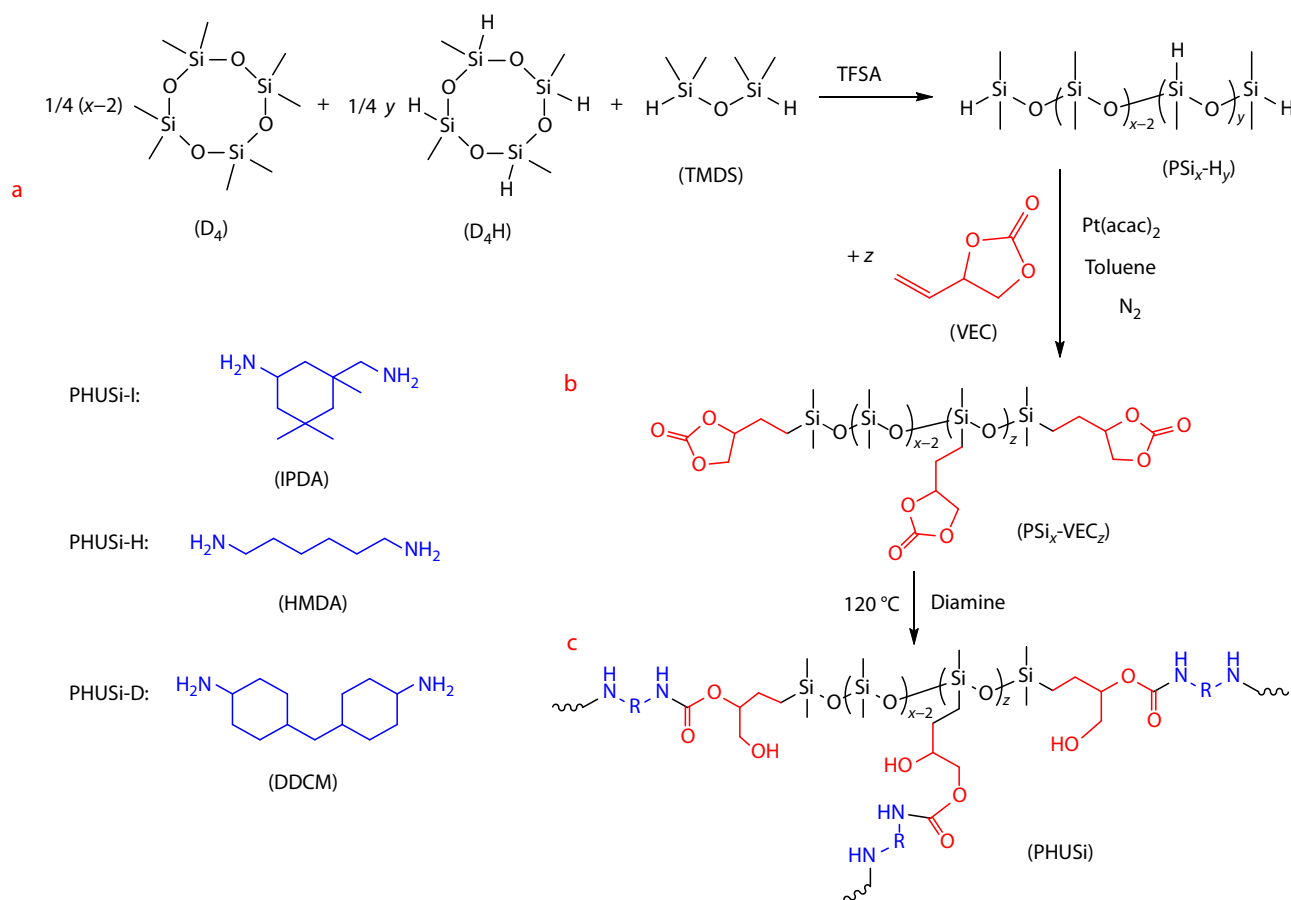


Fig. 1 (a) Synthesis of $\text{PSi}_x\text{-H}_y$ via ring-opening of D_4 and D_4H ; (b) $\text{PSi}_x\text{-VEC}_z$ via hydrosilylation of VEC with $\text{PSi}_x\text{-H}_y$; (c) PHUSi by curing $\text{PSi}_x\text{-VEC}_z$ with three aliphatic diamines.

yield about 86.78%. A series of $\text{PSi}_x\text{-H}_y$ complexes was obtained by varying the molar ratio of $\text{D}_4/\text{D}_4\text{H}$.

Synthesis of $\text{PSi}_x\text{-VEC}_z$

$\text{PSi}_x\text{-VEC}_z$ (z is the theoretical number of $-\text{Si-VEC}$ units) was obtained by hydrosilylation of VEC with $\text{PSi}_x\text{-H}_y$ using a $\text{Pt}(\text{acac})_2$ catalyst. A typical reaction for $\text{PSi}_{14}\text{-H}_4$ preparation is as follows: 52.00 g of $\text{PSi}_{14}\text{-H}_4$ and 0.04 wt% $\text{Pt}(\text{acac})_2$ were dissolved in 50 mL of toluene in a three-neck flask equipped with thermometer and pressure-equalizing dropping funnel and spherical condensing tube. Nitrogen was used to purge the air in the apparatus. Then, 19.00 g (0.17 mol, $\text{C}=\text{C}/\text{Si}-\text{H}$, 1/1) VEC was slowly dripped into the system under 365 nm UV irradiation and stirring, maintaining the temperature at 30 °C. After the addition, the reaction took place for 1 h at 30 °C under a N_2 . The reaction proceeded for another 0.5 h after switching off the UV lamp. The solvent and unreacted raw materials were removed by vacuum distillation to obtain $\text{PSi}_{14}\text{-VEC}_4$. Using the same method, the types of $\text{PSi}_x\text{-H}_y$ and the amount of VEC were changed to obtain a series of $\text{PSi}_x\text{-VEC}_z$.

Synthesis of PHUSi

PHUSi was obtained by curing $\text{PSi}_x\text{-VEC}_z$ with three aliphatic diamines (IPDA, HMDA, and DDCM) *via* a ring-opening reaction between CC and $-\text{NH}_2$. According to the type of amine, PHUSi was named $\text{PHUSi}_x\text{-I}_z$, $\text{PHUSi}_x\text{-H}_z$ and $\text{PHUSi}_x\text{-D}_z$. A typical procedure for $\text{PHUSi}_{14}\text{-I}_4$ preparation is as follows: 10.0 g of $\text{PSi}_{14}\text{-VEC}_4$ (CC: 13.0 mmol), 2 mL of ethanol, 0.372 g of IPDA (2.2 mmol, $\text{CC}/\text{NH}_2=3/1$) and 0.21 g of MQ resins were intensively mixed together and the curing reaction was conducted at 120 °C for 12 h. The mixture was then coated on PET release film. $\text{PHUSi}_{14}\text{-I}_4$ was obtained after the curing reaction was conducted at 120 °C for 24 h. A series of PHUSi was obtained by changing the ratio of CC to $-\text{NH}_2$, the CC or MQ content, and the type of diamine, according to the same process.

Characterization

FTIR and NMR

The chemical structures of $\text{PSi}_x\text{-H}_y$ and $\text{PSi}_x\text{-VEC}_z$ and their precursors were characterized by Fourier transform infrared spectroscopy (FTIR, Tensor 27, Brüker, USA) and ^1H nuclear magnetic resonance (NMR, Advance III, Brüker, USA, 400 MHz). FTIR was performed in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} using KBr tablets. ^1H -NMR spectroscopy was performed in CDCl_3 with dioxane as the internal standard. The hydrogen content (H%) in $\text{PSi}_x\text{-H}_y$ was calculated by integrating the $\text{Si}-\text{H}$ characteristic peak (4.75 ppm) in the ^1H -NMR spectrum, according to Eq. (1):

$$\text{H\%} = \frac{8 \times m_{\text{DO}} \times A_{\text{SiH}}}{M_{\text{DO}} \times m_{\text{PSiH}} \times A_{\text{DO}}} \times 100\% \quad (1)$$

where m_{DO} and m_{PSiH} are the weights of dioxane and $\text{PSi}_x\text{-H}_y$, A_{SiH} and A_{DO} are the integral areas of $\text{Si}-\text{H}$ and eight H in dioxane, respectively; and M_{DO} is the molar mass of dioxane (88 Da).

The cyclocarbonate content (CC%) in $\text{PSi}_x\text{-VEC}_z$ was calculated according to Eq. 2:

$$\text{CC\%} = \frac{8 \times m_{\text{DO}} \times A_{\text{SiCH}_2}}{2 \times M_{\text{DO}} \times m_{\text{PSiVEC}} \times A_{\text{DO}}} \times 100\% \quad (2)$$

where m_{PSiVEC} is the weight of $\text{PSi}_x\text{-VEC}_z$, A_{SiCH_2} is the integral area of two H in $\text{Si}-\text{CH}_2-$, which is formed after the hydrosilylation of $\text{Si}-\text{H}$ with VEC.

The viscosities of $\text{PSi}_x\text{-H}_y$ and $\text{PSi}_x\text{-VEC}_z$ was measured using a rotary viscometer (DV2THBCJO, Brookfield, USA). The number-average molecular weight (M_n) was determined by gel permeation chromatography (GPC, Viscotek TDA305max, Malvern, Britain).

Gel content (GC) and crosslink density (ν_e)

The GC and ν_e of the PHUSi were determined using the equilibrium swelling method.^[24–26] The samples were cut to a specific size (cylindrical disks of 20 mm diameter and 1 mm thickness), and their initial weight (m_{unex} , g) was recorded. The samples were then immersed in containers containing 20 mL of toluene and shaken for 120 h to ensure complete swelling. Subsequently, the samples were removed from the containers, their surface solvent was absorbed using a filter paper, and the swollen mass (m_s , g) was immediately measured. The samples were subjected to vacuum drying at 60 °C overnight and reweighed (m_{ex} , g). The swelling mass ratio (s , %), GC, soluble fraction (w_{sol} , %), and volume fraction (ν) of the polymer in the swollen sample were calculated using Eqs. (3)–(6):

$$s (\%) = \frac{m_s}{m_{\text{unex}}} \times 100 \quad (3)$$

$$\text{GC} (\%) = \frac{m_{\text{ex}}}{m_{\text{unex}}} \times 100 \quad (4)$$

$$w_{\text{sol}} (\%) = \frac{m_{\text{unex}} - m_{\text{ex}}}{m_{\text{unex}}} \times 100 \quad (5)$$

$$\nu = \frac{m_{\text{ex}}/\rho_p}{m_{\text{ex}}/\rho_p + (m_s - m_{\text{ex}})/\rho_s} \quad (6)$$

In Eq. (6), the values of ρ_s (0.865 g/cm^3) and ρ_p (1.088 g/cm^3) represent the solvent density and density of PHUSi (determined by the swelling method), respectively. The average molecular weight of segments between cross-links (M_c , g/mol) and ν_e (mol/cm^3) was calculated using the Flory-Rehner Eq. (7):^[27]

$$\nu_e = \frac{\rho_p}{M_c} = -\frac{1}{V_s} \times \frac{\ln(1 - \nu) + \nu + \chi \nu^2}{\nu^{1/3} - \nu/2} \quad (7)$$

where V_s is the molar volume (106.3 cm^3/mol) and χ is the Flory-Huggins parameter for polymer-solvent interaction (PDMS-toluene, 0.465).

Thermal analysis

The thermal stability of PHUSi was characterized by thermogravimetric analysis (TGA, NETZSCH STA 449F3) in the temperature range of 30–800 °C, with a heating rate of 10 °C/min under N_2 flow.

Viscoelasticity test

A dynamic mechanical analysis (DMA) of PHUSi was conducted using a DMA instrument (DMAQ800, TA Instruments, USA) in the temperature sweep mode. The sample (40 mm × 8 mm × 1 mm, length × width × thickness) was heated from –100 °C to 150 °C at a rate of 5 °C/min and an oscillating frequency of 1 Hz. Viscoelasticity tests of $\text{PHUSi}_{14}\text{-H}_4$, $\text{PHUSi}_{14}\text{-I}_4$ and $\text{PHUSi}_{14}\text{-D}_4$ were carried out in the oscillation mode adopted by a rheometer (HR20, TA Instruments, USA) at 25 °C. The diameter of the test sample was 25 mm, and the thickness of 0.5–1.0 mm is measured using a parallel plate clamp. The angular frequency ranges from 0.01 Hz to 100 Hz.

Adhesive property

The tack adhesion of the PHUSi was determined using the J.

Dow rolling ball method. The tack is the maximum number of balls that remain on the PHUSi with a slope of 30° for more than 5 s. The tack of the PHUSi was also measured quantitatively using a probe adhesion force testing machine (TC-HCN02, Taichang Instruments, China), following a modified version of ASTM D2979. A stainless-steel rod (2.5 mm diameter) was brought into contact with the PHUSi supported on the sample platform at a rate of 3 mm/min under 40 kPa pressure for 1 s, and subsequently breaking the bond formed between the probe and PHUSi at a speed of 1 mm/min. $F_{\max}$ (N) represents the maximum force in the debonding force-distance curves. The work of adhesion (W_a , J/m²) was calculated using Eq. (8), represents the maximum displacement of the adhesive force-distance curve, and $F(x)$ represents the force corresponding to a displacement of x . A is the initial contact area (4.91 mm²) of the probe on the PHUSi surface and a is the maximum distance of the PHUSi.^[18,28]

$$W_a = \frac{\int_0^a F(x) dx}{A} \quad (8)$$

The ability of the PHUSi to remain adhered under a constant load exerted parallel to the bonding surface was determined using a tape shear adhesion tester following GB/T 4851–2014. A strip of PHUSi was applied to a stainless-steel panel or pigskin covering an area of 25 mm × 25 mm. Then, the panel was mounted vertically, and a 500 g weight was attached to the free end of the PHUSi. The holding power, defined as the time elapsed until the tape separated from the panel, was recorded.

The 180° peel strength of the PHUSi was tested using a tensile testing machine (HD-B609B-S, Haida Instrument, China). The glued side of the PET was placed on a PVC plate to ensure that the width of the PET was 25 mm. Rolling back and forth on PET several times with a 2 kg of rubber roller and placed at room temperature for 20 min. The uncontacted end of the PVC board was fixed to the fixture of the tensile testing machine, whereas the other clamp pulled the free end of the PHUSi tape at a rate of 300 mm/min. Using the same method, we tested the peel strength of PHUSi on PET, PP, PE, SU303 stainless steel, glass, and pigskins.

The shear strength of PHUSi was determined by bonding the adhesive film with a stainless-steel substrate or pigskin. The bonding area was 625 mm² (25 mm × 25 mm). The film was rolled back and forth three times with a 2 kg of rubber roller, and the sample was placed at room temperature for 20 min. The uncontacted end of the steel plate was fixed on the fixture, the free end of the tape was fixed on another fixture, and then a 300 mm/min movement was applied away from the steel plate in the direction of the tape. Each sample was tested five times, and the final value was averaged. The effective adhesion energy is the area under the integral of the shear curve.^[18]

Skin irritation test

The skin irritation test was performed according to ISO 10993-10 protocols (details are provided in Fig. S2, Tables S1 and S2 in ESI).

Direct peptide reactivity assay (DPRA)

The DPRA was conducted according to the standard operating procedure mentioned in OECD TG 442C (details are provided in

Table S3 in ESI).^[29]

Application

The ECG signal was measured from a human subject in a standard lead II configuration by placing two tabulated electrodes on the left pectoral region.^[2] A 3.3 V battery was connected to the circuit for the power supply. The output signal of the device was obtained by a Universal Asynchronous Receiver Transmitter (UART) serial interface and then processed by a PC using Starter. To remove noise, a notch filter (50 Hz) and low-pass filter (100 Hz) were used.

The cytotoxicity of PHUSi in HeLa cells was evaluated using a standard MTT assay. Briefly, HeLa cells were seeded in a 96-well plate at a density of approximately 5000 cells per well and cultured for 24 h under standard conditions (37 °C, 5% CO₂ and 95% air). Subsequently, different amounts of PHUSi dissolved in DMEM were added to the wells to achieve final concentrations of 0 (blank control), 100, 300, 500, and 1000 µg/mL, with six parallel replicates for each concentration. After an incubation for 24 h at 37 °C, 10 µL of MTT solution (5.0 mg/mL in PBS, pH 7.4) was added to each well, and the cells were incubated for another 4 h. The culture medium was then removed and 100 µL of DMSO was added to each well. The absorbance at 570 nm was recorded using a Multiskan FC microplate reader (Thermo Fisher Scientific, USA). Cell viability (CV) was calculated using Eq. (9):

$$CV(\%) = \frac{OD}{OD_c} \times 100 \quad (9)$$

where OD and OD_c are the absorbance of treated cells and untreated control cells, respectively, and all OD values were blank-corrected by subtracting the absorbance of the blank well.

RESULTS AND DISCUSSION

Synthesis and Structure Characterization of PSi_x-H_y, PSi_x-VEC_z and PHUSi

PHUSi was synthesized by three steps (Fig. 1). First, PSi_x-H_y was synthesized via the open-ring reaction of D₄ and D₄H using TMDS as the end-capping reagent and TFSA as the catalyst (Fig. 1a). The ratio of hydrogen-containing units to silicone-oxygen units (Si—H/Si—O) in PSi_x-H_y was adjusted by controlling the ratio of D₄/D₄H, and the molecular weight of PSi_x-H_y was adjusted by changing the amount of TMDS. Second, PSi_x-VEC_z was obtained by the hydrosilylation of VEC with PSi_x-H_y (VEC/Si—H = 1/1) using a Pt(acac)₂ catalyst (Fig. 1b). Finally, PHUSi was obtained by the open-ring reaction of the cyclic carbonates of PSi_x-VEC_z with various amines (Fig. 1c).

Structure characterization of PSi_x-H_y

The formulas and characterization data for the precursors PSi_x-H_y are listed in Table S4 (in ESI). With the feed molar ratio of D₄/D₄H increased from 3/0 to 2.25/0.75, the actual molar ratio of Si—H/Si—O (obtained from ¹H-NMR) in PSi_x-H_y increased from 1.7/14 to 4.6/14, and the H% increased from 0.16 % to 0.46% accordingly. The measured ratio of Si—H/Si—O is below the theoretical value, and it is possible that more D₄H is removed as a low-boiling substance during the vacuum process. Additionally, the M_n of the obtained PSi_x-H_y samples remained relatively constant within the range of 3000–3400 Da, with M_w/M_n falling between 1.13 and 1.19. While, their viscosity increased from 1.02 mPa·s to 9.22 mPa·s with the increase of Si—H/Si—O ratio. Si is

less electronegative than H, whereas C is more electronegative. This electronegativity disparity dictates the polarity and orientation of Si—H bonds. The electronegativity difference between Si and H is equivalent to that between C and Br (+0.3).^[30,31] As a result, the polarity of the Si—H bond resembles that of the C—Br bond. An increase in the concentration of Si—H bonds enhances the intermolecular forces, thereby contributing to an increase in the apparent viscosity.

Fig. S3 (in ESI) shows the FTIR spectra of $\text{PSi}_{14}\text{-H}_4$, its monomers D_4 and D_4H , and the end-sealing agent TMDS. In the spectra of D_4H , TMDS, and $\text{PSi}_{14}\text{-H}_4$, the strong absorption bands at 2143 and 919 cm^{-1} originate from the Si—H stretching vibration and bending vibration, respectively. The absorption bands at 2962 and 1262 cm^{-1} correspond to the stretching vibration and symmetric deformation vibration of Si—CH₃. The bands at 1080 and 808 cm^{-1} in D_4H and TMDS correspond to the stretching vibrations of Si—O—Si (disiloxane) and Si—C, respectively.^[9,24] Obviously, the single band at 1080 cm^{-1} exhibits double bands at 1090 and 1025 cm^{-1} in $\text{PSi}_{14}\text{-H}_4$ (Si—O—Si in polysiloxane), indicating that the ring-opening reaction was successful. The FTIR spectra of all $\text{PSi}_x\text{-H}_y$ samples are shown in Fig. S4 (in ESI). Obviously, their spectra are very similar, but with an increase in H%, the peak area ratio of Si—H/Si—CH₃ increases. The above results show that $\text{PSi}_x\text{-H}_y$ was successfully prepared.

Fig. 2(a) shows the $^1\text{H-NMR}$ spectrum of $\text{PSi}_{14}\text{-H}_4$. Fig. S5 (in ESI) shows the $^1\text{H-NMR}$ spectra of monomers D_4 and D_4H , end-capping agent TMDS, and $\text{PSi}_{14}\text{-H}_4$. The chemical shifts of the characteristic peaks are listed in Table S5 (in ESI). In the spectrum of D_4 (Fig. S5 in ESI), a singular Si—CH₃ absorption peak is observed at 0.09 ppm, attributable to the equivalent chemical environment of the eight methyl groups.

Due to the presence of adjacent Si—H bond, the Si—CH₃ absorption peak in D_4H and TMDS is shifted from 0.09 in D_4 to 0.19 ppm and 0.22 ppm, respectively. And the Si—H bond absorption peaks also emerge at 4.23 and 4.75 ppm in the $^1\text{H-NMR}$ spectra of D_4H and TMDS, respectively (Fig. S5 in ESI). The Si—H bond in the D_4H ring experiences a slightly higher electron cloud density because of its location on the ring, which is influenced by the neighboring substituents. Consequently, it is shifted to a higher field and lower chemical shift compared to the Si—H bond in TMDS and linear $\text{PSi}_{14}\text{-H}_4$. In the $^1\text{H-NMR}$ spectra of $\text{PSi}_{14}\text{-H}_4$ (Fig. 2(a)), the proton peak for

$\text{H}_3\text{C—Si—CH}_3$ is observed at 0.09 ppm (H1),^[32] the proton peak for H—Si—CH_3 at 0.20 ppm (H2, H4),^[22] the proton peak of the internal standard dioxane at 3.73 ppm,^[33] and the proton peak for Si—H at 4.75 ppm (H3, H5).^[24] Fig. S6 (in ESI) presents the $^1\text{H-NMR}$ spectra of various $\text{PSi}_x\text{-H}_y$ samples. It is evident that as the feed D_4H content increases, $A_{\text{SiH}}/A_{\text{DO}}$ also increases, and H% is obtained using Eq. (1) and listed in Table S4 (in ESI).

Structure characterization of $\text{PSi}_x\text{-VEC}_z$

A series of $\text{PSi}_x\text{-VEC}_z$ was prepared by the hydrosilylation of $\text{PSi}_x\text{-H}_y$ with VEC at 1/1 of VEC/Si—H in the molar. According to the method described in Eq. (2), the CC mol% was estimated by integrating the peak area of Si—CH₂ (Ha, Hb) in $^1\text{H-NMR}$ spectrum (Fig. 2a) with dioxane as the internal standard, and the results were listed in Table S6 (in ESI). As the amount of VEC added increased, CC mol% increased from 0.09% in $\text{PSi}_{14}\text{-VEC}_2$ to 0.15% in $\text{PSi}_{14}\text{-VEC}_5$. The ratio of VEC/Si—O increased from 1.2/14 to 2.3/14, but was lower than that of Si—H/Si—O. This was because the conversion of the hydrosilylation reaction was incomplete. The M_n of $\text{PSi}_x\text{-VEC}_z$ underwent a reduction following hydrosilylation when compared with $\text{PSi}_x\text{-H}_y$. This decline is likely attributable to a surge in molecular polarity^[34] which in turn intensifies the intermolecular forces between $\text{PSi}_x\text{-VEC}_z$ and the separation matrix. Consequently, the retention time of $\text{PSi}_x\text{-VEC}_z$ within the separation medium was prolonged.

Fig. S7 (in ESI) shows the FTIR spectra of $\text{PSi}_{14}\text{-VEC}_4$, along with its parent compounds, $\text{PSi}_{14}\text{-H}_4$ and VEC. The VEC spectrum exhibits several unique absorption features: the C—H stretching vibration band attributed to the $\text{CH}_2=\text{CH—}$ group appears at 3099 cm^{-1} , with the asymmetric and symmetric stretching vibrations of the $-\text{CH}_2$ group in the ring represented by the bands at 2993 and 2920 cm^{-1} , respectively. The characteristic absorption band for the C=O stretching vibration of the cyclic carbonyl group was observed at 1803 cm^{-1} .^[34–36] Additionally, the band at 1382 cm^{-1} is associated with the bending vibration absorption of CH_2 , and the bands at 1169 and 1068 cm^{-1} correspond to the symmetric and asymmetric stretching vibrations of the C—O—C linkage.^[21,25] In the spectrum of $\text{PSi}_{14}\text{-VEC}_4$, the disappearance of the $\text{CH}_2=\text{CH—}$ stretching vibration band at 3099 cm^{-1} is significant. Similarly, the absence of absorption peaks related to the Si—H bond at 2143 and 919 cm^{-1} is noteworthy.

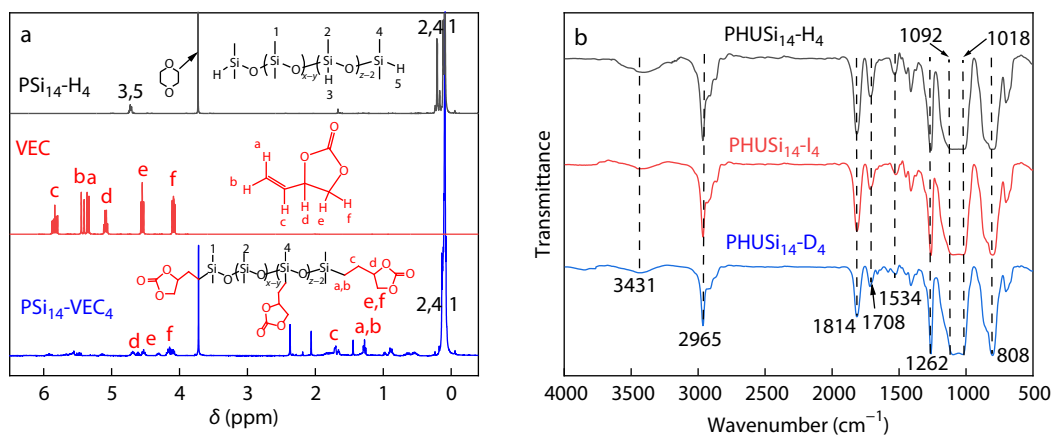


Fig. 2 (a) $^1\text{H-NMR}$ spectra of $\text{PSi}_{14}\text{-H}_4$, VEC, and $\text{PSi}_{14}\text{-VEC}_4$; (b) FTIR spectra of PHUSi cured with different amines (NH_2/CC molar ratio of 1/3).

thy. A distinct absorption peak was observed for the C=O stretching vibration at 1814 cm^{-1} . These findings indicated that the double bond in VEC reacted completely with the Si—H bond, leading to the integration of the cyclic carbonate group into the $\text{PSi}_{14}\text{-H}_4$ chain and the formation of $\text{PSi}_{14}\text{-VEC}_4$. Fig. S8 (in ESI) shows the FTIR spectra of the entire series of $\text{PSi}_x\text{-VEC}_z$ samples. It is apparent that the peaks in all the $\text{PSi}_x\text{-VEC}_z$ spectra are consistent, confirming the successful synthesis of $\text{PSi}_x\text{-VEC}_z$.

Fig. 2(a) also displays the $^1\text{H-NMR}$ spectra of VEC and $\text{PSi}_{14}\text{-VEC}_4$, with the chemical shifts of their characteristic peaks provided in Table S7 (in ESI). In the $^1\text{H-NMR}$ spectrum of VEC, the two proton peaks of CH_2 (Ha, Hb) were observed at $\delta=5.35$ and 5.43 ppm, while the peak of $-\text{CH}=$ (Hc) was located at $\delta=5.84$ ppm.^[37] Following hydrosilylation, the double bond was converted to a single bond, and consequently, the double bond peaks vanished in the $^1\text{H-NMR}$ spectrum of $\text{PSi}_{14}\text{-VEC}_4$. Instead, two new proton peaks emerged at $\delta=1.28$ (Ha, Hb) and 1.77 (Hc). The proton peaks of $-\text{O}-\text{CH}_2-$ (He, Hf) in the cyclic carbonate ring of VEC were observed at $\delta=4.08$ and 4.54 ppm,^[19,36] appearing as double peaks due to stereochemical conformations, and these shift to 4.01 and 4.46 ppm in the $\text{PSi}_{14}\text{-VEC}_4$ spectrum after the addition. The proton peak of $-\text{O}-\text{CH}-$ (Hd) in the cyclic carbonate ring of VEC was observed at $\delta=5.08$ ppm.^[21] After addition, the adjacent double bond is converted to a single bond, influenced by the shielding effect of the electron cloud, causing the chemical shift of $\text{PSi}_{14}\text{-VEC}_4$ to move to the high-field region at 4.69 ppm. Notably, after the addition, the Si—H peak disappeared in the $^1\text{H-NMR}$ spectrum of $\text{PSi}_{14}\text{-VEC}_4$, and the associated $\text{H}-\text{Si}-\text{CH}_3$ shifted to the high-field region, coinciding with the $\text{Si}-\text{CH}_3$ (H1) in dimethylsiloxane at $\delta=0.09$ ppm. Fig. S9 (in ESI) shows $^1\text{H-NMR}$ spectra of all $\text{PSi}_x\text{-VEC}_z$. The peaks of all $\text{PSi}_x\text{-VEC}_z$ samples were consistent. These results indicated that $\text{PSi}_x\text{-VEC}_z$ was successfully synthesized.

Structure characterization of PHUSis

A series of PHUSis was prepared by the ring-opening reaction of polysiloxane-containing cyclic carbonate ($\text{PSi}_x\text{-VEC}_z$) with three diamine curing agents, including IPDA, HMDA, and DDCM (Fig. 1c). The mechanism of NIPU formation *via* ring-opening between the amine and cyclic carbonate is relatively clear.^[20] First, the electron-rich amine group attacks the electron-deficient carbonyl carbon atom in the cyclic carbonate and forms a tetrahedral intermediate. Then, under the influence of the attack of another amino group, the tetrahedral intermediate is deprotonated, and the strong electron absorption effect of nitrogen atoms causes the carbon-oxygen bond to break, resulting in the formation of NIPU (Fig. S10 in ESI).

Fig. 2(b) and Fig. S11 (in ESI) present the FTIR spectra of $\text{PHUSi}_{14}\text{-H}_4$, $\text{PHUSi}_{14}\text{-D}_4$, $\text{PHUSi}_{14}\text{-I}_4$, and a series of $\text{PHUSi}_{14}\text{-I}_z$ samples with different CC contents and NH_2/CC molar ratios. The absorption bands at 2965 and 1262 cm^{-1} correspond to the stretching vibration and symmetric deformation vibration of $\text{Si}-\text{CH}_3$. The bands at 1092 and 1018 cm^{-1} are the stretching vibrations of $\text{Si}-\text{O}-\text{Si}$ in polysiloxane. As shown in Fig. 2(b) and Fig. S11(a) (in ESI), the cyclic carbonate band (C=O stretching) of $\text{PSi}_x\text{-VEC}_z$ at 1814 cm^{-1} still existed because the CC content was excessive (molar ratio of $\text{NH}_2/\text{CC}=1/3$). The characteristic peaks of the urethane band

(C=O, N—H stretching vibrations and NH deformation vibration) appeared at 1708, 3431, and 1534 cm^{-1} .^[35,38–40] The OH stretching vibration peak was also observed around 3400 cm^{-1} , overlapping with the peak of the NH group. In Fig. S11(b) (in ESI) as the NH_2/CC molar ratio increased, the intensity of the band at 1814 cm^{-1} gradually decreased. When the NH_2/CC molar ratio was 1/1, this peak disappeared, and the peak at 1708 cm^{-1} gradually increased. When the NH_2/CC molar ratio was 1/5, the NH_2 content was low, and there were no characteristic peaks of the urethane band. These results indicated the successful formation of urethane units.

Adhesive Properties

Effect of CC content and $-\text{NH}_2/\text{CC}$ molar ratio

The CC in silicone oil serves a dual role: it reacts with amines to form hydroxyl carbamate groups, which act as crosslinking points for PHUSi, while its polar nature enhances the overall polarity of PHUSi, thereby improving cohesion and adhesion to substrates. Consequently, investigating the influence of the CC content and $-\text{NH}_2/\text{CC}$ molar ratio on the adhesive properties of PHUSi is essential.

The 180° peel strength, holding power, and shear strength of $\text{PHUSi}_{14}\text{-I}_z$ with different CC content (cured from $\text{PHUSi}_{14}\text{-VEC}_z$ using IPDA at a fixed NH_2/CC molar ratio of 1/3) were systematically evaluated (Fig. 3a). The tack ball number, probe tack maximum force, and work of adhesion were also evaluated (Fig. 3b). The results demonstrate that as the CC content increased, the shear strength correspondingly increased. However, the initial tack, holding power, 180° peel strength, tack force and the work of adhesion initially rise significantly, reaching peak values at an optimal CC content of 0.13 mol% ($\text{PHUSi}_{14}\text{-I}_4$), before gradually declining. When the CC content was held constant and the $-\text{NH}_2/\text{CC}$ molar ratio was varied from 1/1 to 1/5, the initial tack, holding power, 180° peel strength, shear strength, tack force, and work of adhesion exhibited a similar trend, initially increasing and then decreasing (Figs. S12a and S12b in ESI). Notably, these properties achieved optimal values at an $-\text{NH}_2/\text{CC}$ molar ratio of 1/3.

These observations can be attributed to the crosslinking density (v_e) of the PHUSi. The GC and v_e values of the PHUSi were determined, and the results are listed in Table S8 (in ESI). The GC and v_e values of $\text{PHUSi}_{14}\text{-I}_2$ and $\text{PHUSi}_{14}\text{-I}_3$ are 0, as these two PSA films are broken and swollen after immersion in toluene. When the $-\text{NH}_2/\text{CC}$ molar ratios of $\text{PHUSi}_{14}\text{-I}_4$ were 1/4 and 1/5, PHUSi was not crosslinked, and the product was not completely cured. Thus, there are no data for $\text{PHUSi}_{14}\text{-I}_2$, $\text{PHUSi}_{14}\text{-I}_3$ and $\text{PHUSi}_{14}\text{-I}_4$ (the $-\text{NH}_2/\text{CC}$ molar ratio 1/4, 1/5) in Table S8 (in ESI). In PSAs, a lower v_e typically results in a weaker cohesive strength, characterized by reduced tensile strength and elastic modulus, which compromises the integrity of the adhesive layer. Consequently, the shear strength, 180° peel strength, and holding power were adversely affected at low crosslinking levels.^[41] As v_e increased (Table S8 in ESI), the storage modulus (G') from the sweep temperature measurement increased (Fig. S13a in ESI), thereby enhancing the cohesive strength of the adhesive layer and significantly improving its overall performance. However, excessive cross-linking significantly increased the storage modulus and reduced the loss factor (Fig. S13b in ESI), which im-

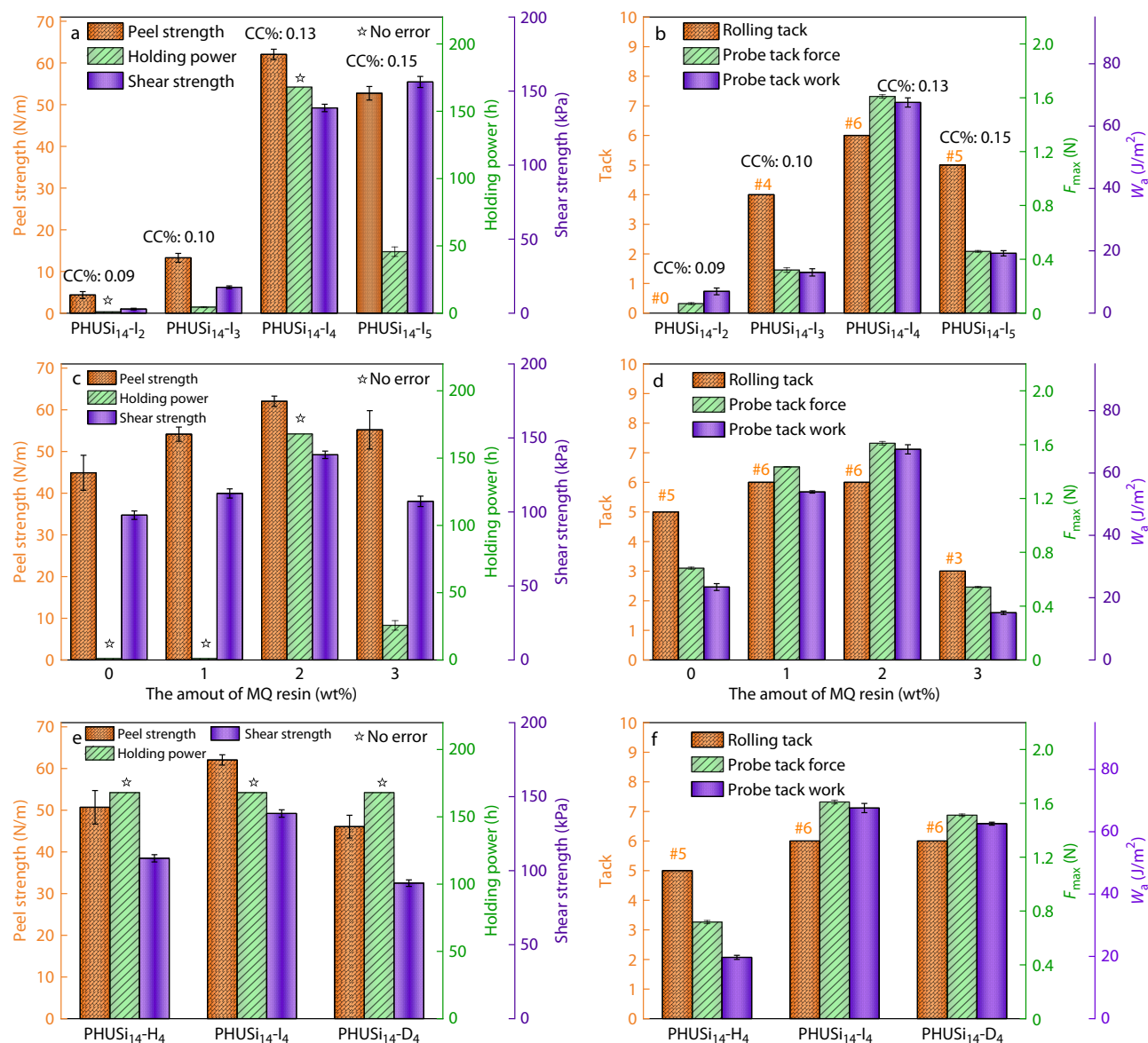


Fig. 3 (a, b) 180° peel strength on PVC, holding power, shear strength, the rolling ball test, the maximum probe tack force and the work of adhesion of PHUSi₁₄-L₂ with different CC content; (c, d) those properties of PHUSi₁₄-L₄ with different MQ resin contents of PHUSi₁₄-L₄ (PHUSi₁₄-VEC₂ cured with IPDA at a fixed $-\text{NH}_2/\text{CC}$ molar ratio of 1/3); (e, f) those properties of PHUSi₁₄-H₄, PHUSi₁₄-L₄, PHUSi₁₄-D₄ (PHUSi₁₄-VEC₄ cured with different diamines).

pairs the ability of PSA to wet substrates, reduces interfacial adhesion forces, and leads to a decline in the 180° peel strength and initial tack.^[42] Thus, when the CC content increased, the shear strength improved markedly with increased crosslinking, and the holding power, 180° peel strength, and initial tack exhibited optimal values before decreasing with further crosslinking. PHUSi₁₄-L₄ ($-\text{NH}_2/\text{CC}=1/3$) exhibited a single peak (-53°C) in the $\tan\delta$ curve, while PHUSi₁₄-L₅ ($-\text{NH}_2/\text{CC}=1/3$) exhibited two peaks (-52°C and -20°C) (Fig. S13b in ESI). This suggests that at lower v_e values of PHUSi, the molecular chains possess enhanced mobility, which facilitates favorable compatibility between the soft segment of polysiloxane and hard segment of carbamate. However, as v_e increases, the mobility of the molecular chains is impeded and the interaction force between the hard seg-

ments is enhanced, leading to microphase separation between the soft segments of polysiloxane and the hard segments of carbamate.^[43]

Effect of MQ

The application of MQ resin in PSA has significantly improved its performance, including increased adhesion to various surfaces, heat resistance, and cohesion strength.^[44] In addition, MQ resin optimizes the rheological properties of the pressure-sensitive adhesive, allowing it to show better adaptability during coating and use, and enhances weather resistance, such as resistance to UV light and humidity changes, thereby extending the service life of the product.^[22,23]

The 180° peel strength, holding power, and shear strength of PHUSi₁₄-L₄ with different MQ resin contents were systemati-

cally evaluated (Fig. 3c). The tack ball number, probe tack maximum force, and work of adhesion were systematically evaluated (Fig. 3d). With increasing MQ content, the initial tack, probe tack maximum force, and work of adhesion initially increased and reached a peak at an MQ concentration of 2 wt%. The holding power was higher than 168 h at an MQ concentration of 2 wt% and lower than that at 48 h at other concentrations. This behavior originates from the intrinsically low polarity of the MQ resin, which weakens its interfacial interaction with the substrate; a judicious MQ loading stiffens the polymer network and suppresses chain slippage, thereby increasing the holding power. However, excessive MQ content, owing to its poor compatibility with the polymer matrix, introduces stress-concentration sites and consequently leads to a pronounced decline in the holding power.^[44] When the content of the MQ resin of PHUSi₁₄-I₄ ranged from 0 wt% to 2 wt%, the 180° peel strength and shear strength slightly increased and then decreased with increasing MQ resin content. The GC and v_e values of these PHUSi were also determined, and the results are listed in Table S8 (in ESI). The v_e of PHUSi₁₄-I₄ with different contents of MQ resin was similar, from 1.13×10^{-3} mol/cm³ to 1.24×10^{-3} mol/cm³. It can be seen that the crosslinking density of PHUSi decreases after adding the MQ resin, which has little effect on its peel strength and shear strength.

Effect of aliphatic diamines

In traditional PU systems, the structure of the isocyanates plays a critical role in determining the performance of the resulting PU. To investigate this further, three different aliphatic diamines, HMDA, IPDA, and DDCM, were employed as curing agents for PHUSi₁₄-VEC₄.

The 180° peel strength, shear strength, and holding power of the resulting PHUSi₁₄-I₄, PHUSi₁₄-H₄, and PHUSi₁₄-D₄ samples were systematically evaluated (Fig. 3e). The results revealed that all the samples exhibited excellent holding power (exceeding 168 h), high 180° peel strength (>46 N/m), and shear strength (>91 KPa). The 180° peel strength of PHUSi₁₄-I₄ (62 N/m) was notably higher than that of PHUSi₁₄-H₄ (51 N/m), which surpassed that of PHUSi₁₄-D₄ (46 N/m). This variation in performance can be attributed to the structural differences between the curing agents. HMDA has a long alkyl chain and reduces steric hindrance. Therefore, PHUSi₁₄-H₄ had a higher v_e (Table S8 in ESI), leading to a relatively higher storage modulus in PHUSi₁₄-H₄ (Fig. S14a in ESI), which impairs its wettability on the substrate and consequently diminishes its adhesive performance. However, the higher rigidity of DDCM led to a lower v_e , with a relatively lower storage modulus (Fig. S14a in ESI), resulting in reduced cohesive strength and adhesive performance. PHUSi₁₄-I₄ exhibited moderate v_e and chain mobility, which enabled it to achieve excellent interfacial adhesion, sufficient cohesive strength, and long-term stability of the adhesive. The $\tan\delta$ curves (Fig. S14b in ESI) indicate that T_g values of PHUSi₁₄-H₄, PHUSi₁₄-I₄ and PHUSi₁₄-D₄ are -59, -53, -65 °C, which are the structural bases for their sensitivity. The tack ball number, probe tack maximum force, and work of adhesion of PHUSi₁₄-I₄, PHUSi₁₄-H₄, and PHUSi₁₄-D₄ were evaluated systematically (Fig. 3f). The results revealed that the data of PHUSi₁₄-I₄ and PHUSi₁₄-D₄ were similar and higher than those of PHUSi₁₄-H₄. The

maximum probe tack force of PHUSi₁₄-I₄ and PHUSi₁₄-D₄ was 1.61 and 1.51 N, respectively, but that of PHUSi₁₄-H₄ was only 0.72 N. This can be attributed to the highest v_e of PHUSi₁₄-H₄ (Table S8 in ESI), leading to a reduction in adhesive toughness and interfacial adhesion performance.^[18]

The 180° peel strengths of PHUSi₁₄-I₄, PHUSi₁₄-H₄, and PHUSi₁₄-D₄ on the different substrates were evaluated (Fig. 4a). The results indicate that the 180° peel strength of PHUSi on various substrates follows the order PVC > Glass > PET > Steel > PP > PE. Adhesive-substrate interactions are complex, where interfacial bonding is governed by multiple contributing factors, including but not limited to surface free energy, chemical compatibility, surface morphology, and mechanical interlocking effects. PHUSi exhibited outstanding adhesive performance on the skin, with PHUSi₁₄-I₄ showing superior bonding properties compared to PHUSi₁₄-H₄ and PHUSi₁₄-D₄ (Fig. S15 in ESI). Specifically, PHUSi₁₄-I₄ achieves a peel strength of 76.5 N/m, a shear strength of 177 kPa, and an exceptional holding power exceeding 168 h. These results highlight the strong interfacial adhesion and robust cohesion strength of PHUSi₁₄-I₄, making it highly suitable for skin-contact applications, such as medical adhesives or wearable devices. By comparing PHUSi with other commercial medical-grade organic silicone pressure-sensitive adhesives, the 180° peel strength of PHUSi₁₄-I₄ is greater than that of other soft-skin silicones, and achieved 62.1 N/m on PVC, 76.5 N/m on skin (Table S9 in ESI). We also compared the peel strength of PHUSi₁₄-I₄ with that of reported adhesives used for on-skin wearables (Table S10 in ESI). Our material reaches 76.5 N/m (first entry in the table) and outperforms or matches several representative systems (68.8^[45], 60.0^[46], 41.0^[47], 40.0^[48], and 28.0^[49] N/m), indicating a strong potential for robust on-skin adhesion. This not only ensures sufficient adhesion strength, but also results in less pain during removal and reduces skin damage. The shear strength and effective adhesion energy of PHUSi₁₄-I₄, PHUSi₁₄-H₄, and PHUSi₁₄-D₄ (Fig. 4b) demonstrate that PHUSi₁₄-I₄ has the highest value. This variation in performance can also be attributed to the structural differences between the three curing agents and v_e .

To explore the adhesion and debonding behavior of the PSAs, the storage modulus and loss modulus of PHUSi were obtained using the amplitude scanning mode in a rheometer at 25 °C. The resulting dynamic modulus of the PHUSi is shown in Fig. 4(c). Adhesion occurs when an external force is applied at a relatively low frequency, whereas deadhesion occurs when a high-frequency external force is applied.^[50] PHUSi₁₄-I₄ and PHUSi₁₄-H₄ show higher storage moduli than loss moduli; however, PHUSi₁₄-D₄ shows a higher storage modulus than loss modulus only at higher frequencies, which shows that elastic behavior is dominant. This elasticity provides sufficient cohesiveness for PSAs so that PSAs can withstand mechanical stress during the stripping process. Taking the loss modulus as the abscissa and the storage modulus as the ordinate, the viscoelastic window of the corresponding PHUSi was constructed, as shown in Fig. 4(d). At 25 °C and 100 s⁻¹ frequencies, the storage modulus of all PHUSi samples is less than 3.3×10^5 Pa, which is in accordance with the Dahlquist criterion.^[51,52] PHUSi₁₄-I₄ and PHUSi₁₄-D₄ can also be classified as removable PSA because the majority of their

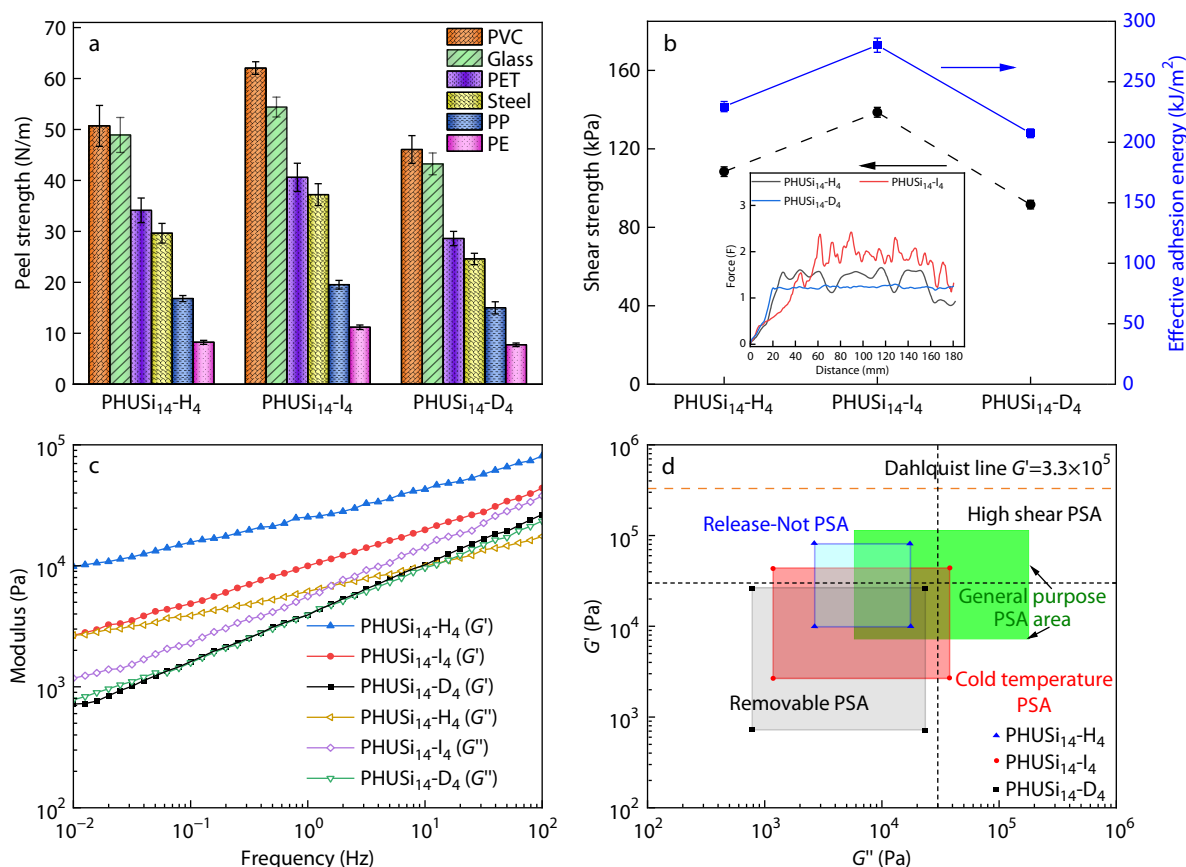


Fig. 4 (a) 180° peel strength of PHUSi₁₄-H₄, PHUSi₁₄-I₄ and PHUSi₁₄-D₄ on different substrates; (b) Shear strength and effective adhesion energy and (c) storage modulus (G') and loss modulus (G'') of PHUSi₁₄-H₄, PHUSi₁₄-I₄ and PHUSi₁₄-D₄; (d) Viscoelastic window of PHUSi.

windows are located in the bottom left quadrant. While PHUSi₁₄-H₄ was evenly distributed in both the first and third quadrants, its ability to wet the substrate surface was the weakest, and its initial adhesion performance was poor.

Thermal Properties

The influence of varying the MQ resin content on the performance of PHUSi₁₄-I₄ was analyzed using thermogravimetric curves (Figs. S16a and S16b, Table S11 in ESI). Obviously, when the MQ resin was not present, the initial decomposition temperature ($T_{5\%}$) of PHUSi₁₄-I₄ was 255 °C, the final residual carbon content (C_{700}) was only 2.8%, and its decomposition was divided into two stages, namely 311 °C ($T_{\max}^{1st}$) and 399 °C ($T_{\max}^{2nd}$). When 2 wt% MQ resin was added, its $T_{5\%}$ increased to 269 °C, C_{700} increased to 35.3%, and its decomposition process included three stages: $T_{\max}^{1st}$ was 339 °C, $T_{\max}^{2nd}$ was 436 °C, and $T_{\max}^{3rd}$ was 695 °C. The cleavage of cyclic carbonate, urethane bonds, and Si—CH₃ mainly occurs in the first stage. The second stage is the decomposition of the Si—O—Si in the cross-linked network with a low cross-linking density. The third stage was the decomposition of the Si—O—Si in MQ resin.^[44] The values of $T_{\max}^{1st}$ and $T_{\max}^{2nd}$ increased while their lost mass decreased, suggesting that the MQ resin enhanced system cohesion through physical barriers and hydrogen bonding interactions, thereby slowing the release of small molecules, hindering thermal decomposition, and increasing the residual carbon content. However, excessive MQ resin addition can reduce the thermal stability of the sample, possibly because MQ resin does not

participate in the formation of the PSA crosslinking network, leading to deterioration in the sample performance.^[53]

The thermal stabilities of PHUSi₁₄-H₄ and PHUSi₁₄-D₄ were also evaluated (Figs. S16c, S16d, and Table S11 in ESI). Compared with PHUSi₁₄-I₄, their TGA and DTG curves were basically the same. It is obvious that the thermal stability of PHUSi₁₄-H₄ ($T_{5\%}$, 259 °C; $T_{30\%}$, 363 °C) is slightly lower than that of PHUSi₁₄-I₄, whereas that of PHUSi₁₄-D₄ ($T_{5\%}$, 279 °C; $T_{30\%}$, 373 °C) is slightly higher. This might be due to the fact that the rigidity of DDCM is greater than that of IPDA and HMDA.

Clinical Validation of PHUSi for Wearable Biosensor Applications

We conducted comprehensive *in vivo* testing to evaluate the performance of the PHUSi as a medical-grade adhesive for wearable biosensors. In clinical validation studies, an electrocardiogram (ECG) sensor was securely attached to a volunteer's left precordial region using a PHUSi adhesive and interfaced with a flexible printed circuit (FPC) board. Continuous 24 h electrophysiological monitoring in a standard lead II configuration demonstrated excellent signal acquisition through UART serial communication, with subsequent signal processing performed using Starter software (Fig. 5a). The recorded ECG waveforms exhibited exceptional fidelity, clearly displaying characteristic components including distinct P-waves (0.08–0.12 s duration), prominent QRS complexes (0.06–0.10 s duration), and well-defined T-waves (0.10–0.25 s duration) (Figs. 5b and 5c).

Complementary *in vitro* cytotoxicity assessment via MTT as-

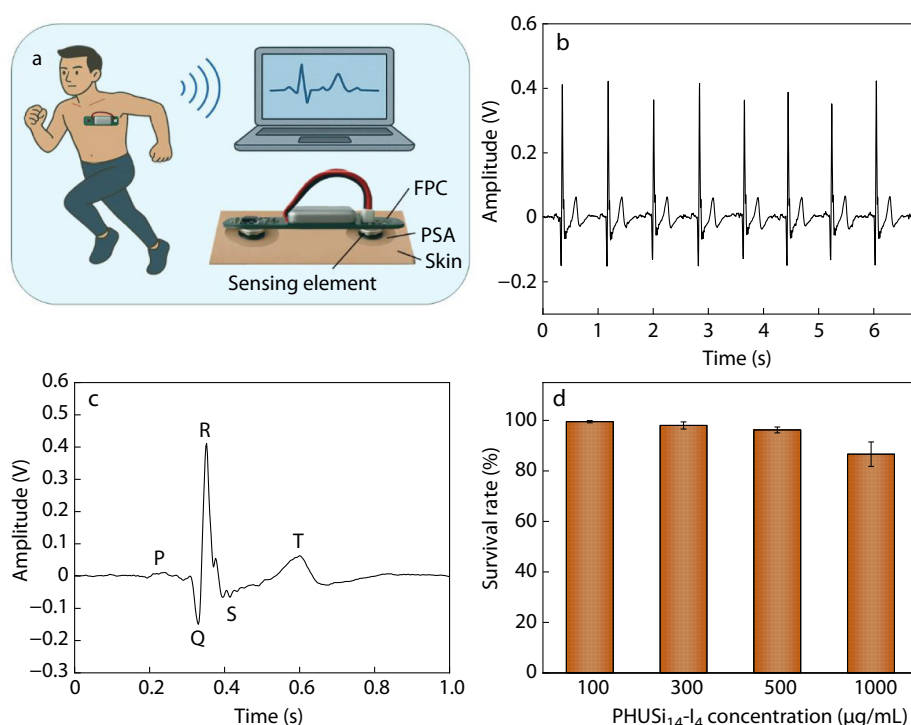


Fig. 5 (a) Schematic representation of the attachment of the flexible ECG sensor to the skin; (b) Example of ECG signals from a volunteer's heart; (c) A detailed view that shows the expected P, QRS-complex, and T waveforms; (d) Cytotoxic effect of PHUSi on HeLa cells at different concentrations.

say revealed outstanding biocompatibility, with HeLa cell viability exceeding 80% across all tested concentrations (0.1–10 mg/mL) (Fig. 5d). In a single-exposure dermal irritation study, the test animals were evaluated for erythema and edema at 24, 48, and 72 h post-application (Fig. S17 and Table S12 in ESI) using the Draize criteria. At 1 h post-removal, transient erythema was observed in one animal; all others exhibited responses comparable to those of the saline control (no edema detected). The Primary Irritation Index (PII) was calculated by summing the scores across all time points and normalizing them to the total observations. The resultant PII of 0 classifies the test article as practically non-irritating under the study conditions. Cysteine (Cys) and lysine (Lys) channels were used for the DPRA of PHUSi. Fig. S18 (in ESI) are their standard curves, and the linear regression coefficients, R^2 are all greater than 0.9999. In the Cys channel (Table S13 in ESI), the positive control exhibited a depletion of $75.90\pm0.79\%$ ($SD<14.9\%$), validating assay performance. Control peptides A (0.5030 mmol/L) and C (0.4927 mmol/L) consistently fell within the target range (0.45–0.55 mmol/L), while the combined peak-area coefficient of variation (CV) for controls B+C (0.43%) confirmed high precision ($<15\%$ threshold). Test sample reactivity was minimal, with a depletion of $1.34\pm0.35\%$ ($SD<14.9\%$). Similarly, in the Lys channel (Table S14 in ESI), the positive control demonstrated $43.78\pm0.35\%$ depletion ($SD<11.6\%$; within 40.2%–69.4% reference range), and control peptides A (0.5015 mmol/L) and C (0.4906 mmol/L) met concentration specifications (0.45–0.55 mmol/L). The combined B+C peak-area CV (0.62%) and sample depletion ($1.06\pm0.68\%$, $SD<11.6\%$) further supported assay reproducibility and negligible reactivity. Together, these results confirm robust experi-

mental conditions and reliable test outcomes, with the observed reactivity classified as none to minimal.

These collective findings demonstrate that the PHUSi adhesive maintains: (1) reliable long-term adhesion for continuous monitoring applications, (2) uncompromised signal integrity for accurate clinical diagnostics, and (3) excellent cytocompatibility for safe, prolonged skin contact, establishing its strong potential for next-generation wearable medical devices.

CONCLUSIONS

In summary, we present an approach for the design and preparation of Si-PSAs for skin-contact applications. A non-toxic, non-isocyanate polyurethane method was used to introduce urethane bonds into a polysiloxane system, thereby improving the adhesive performance. Silicone oils with various CC groups were synthesized, uniformly mixed with diamines, and cured in an oven to form PHUSi. The chemical structures of the intermediates ($\text{PSi}_x\text{-H}_y$ and $\text{PSi}_x\text{-VEC}_2$) and PHUSi were characterized, and the bonding properties were evaluated. An $\text{-NH}_2/\text{CC}$ molar ratio of 1/3 yielded the optimal peel strength. Increasing the CC content moderately improved cohesion and polarity, but excessive CC content reduced wettability due to high crosslinking density. Adding about 2 wt% MQ resin enhanced the holding performance, whereas excess amounts lowered the crosslink density and degraded the performance. Among diamines, PHUSi₄-I₄ achieved balanced crosslinking, exhibiting the highest peel strength (76.5 N/m on skin) and probe tack force (1.61 N). The silicone-based adhesive successfully recorded real-time ECG signals without causing skin irritation, allergies, or redness.

Thus, this material shows promise for skin-adhesive applications, such as tapes, wound dressings, and wearable devices.

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/s10118-025-3503-7>.

Data Availability Statement

Data supporting the findings of this study are available from the corresponding author upon reasonable request.

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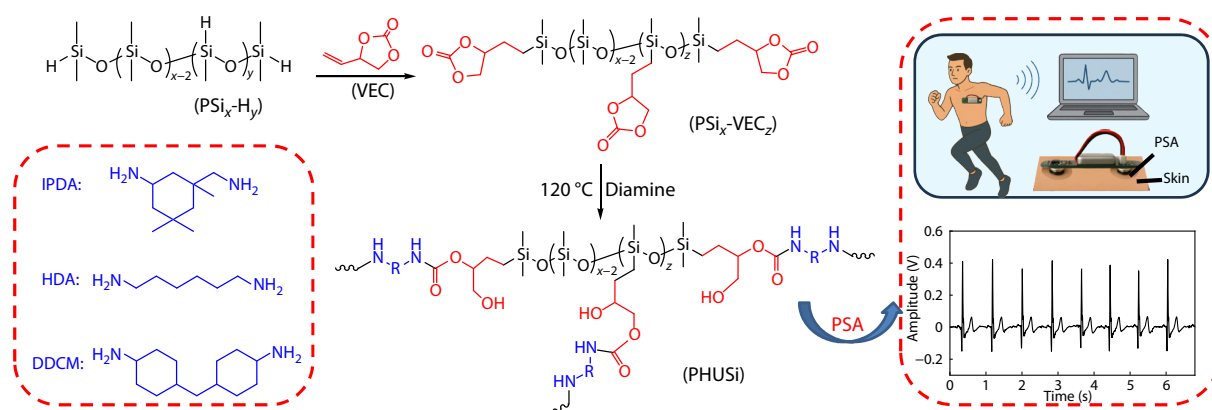
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Graphical Abstract

Poly(hydroxy urethane-siloxane) Pressure-sensitive Adhesive: Synthesis, Characterization and Its Usage for Skin-contact Sensors

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Poly(hydroxy urethane-siloxane) pressure-sensitive adhesives (PHUSi) were synthesized through the reaction of cyclic carbonate-functionalized polysiloxanes with diamines. PHUSi exhibits high biocompatible and adhesive performance, suitable for medical applications, such as flexible electrocardiogram devices.



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