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Enhancement of the adhesion of polysiloxane-based adhesives through catechol functionalization†

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In this study, polysiloxane-based adhesives were prepared by introducing a catechol component into the side chains of copolymers comprising polydimethylsiloxane (PDMS) and ammonium-functionalized polysiloxane components *via* urea bonds. Aluminum plates were adhered using these polysiloxanes containing PDMS and catechol-functionalized polysiloxane (PS-Ph(OH)$_2$) components at the compositional ratios of 9:1, 8:2, 7:3, 6:4 and 5:5 (PDMS-PS-Ph(OH)$_2$ (9:1, 8:2, 7:3, 6:4 and 5:5), respectively), and adhesion was evaluated *via* tensile shear tests at room temperature. The aluminum plates adhered using PDMS-PS-Ph(OH)$_2$ (8:2, 7:3, 6:4 and 5:5) exhibited high adhesive strength, withstanding tensile shear stresses of 12.7–21.7 MPa. Moreover, PDMS-PS-Ph(OH)$_2$ (8:2 and 7:3) maintained strong adhesion under impact loads. Furthermore, when a 5 kg weight was suspended from the aluminum plates adhered using PDMS-PS-Ph(OH)$_2$ (8:2 and 7:3) and the entire assembly was subsequently heated in an oven, the plates did not peel off until the temperature reached 180 °C and 190 °C, respectively, indicating that adhesion was maintained even at relatively high temperatures. Additionally, adherend plates possessing different thermal expansion coefficients, such as aluminum and stainless-steel plates, were adhered using PDMS-PS-Ph(OH)$_2$ (8:2 and 7:3). Thereafter, a 5 kg weight was suspended from the plates, and the temperature was cycled between room temperature and 150 °C. Consequently, the plates did not peel off, suggesting that PDMS-PS-Ph(OH)$_2$ (8:2 and 7:3) could effectively achieve adhesion between dissimilar materials.

Introduction

Mussels can strongly adhere to various organic and inorganic surfaces because of the functionality of an adhesive protein excreted by them. This protein contains catecholic amino acids, such as 3,4-dihydroxy-L-phenylalanine (DOPA),[1–4] which can adhere to both dry and wet surfaces. The catechol component of DOPA is involved in adhesion and serves two func-

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†Electronic supplementary information (ESI) available: Experimental section, ^{1}H NMR spectra of PDMS-PS-NH$_3$Cl and lauroyl-protected PDMS-PS-NH$_3$Cl, GPC curves of lauroyl-protected PDMS-PS-NH$_3$Cl, fracture surface information (photographs, SEM and EDX) of aluminum plates adhered using PDMS-PS-Ph(OH)$_2$ (7:3), stress–strain curves of PDMS-PS-NH$_3$Cl, TGA and DSC data of the cured PDMS-PS-Ph(OH)$_2$ (7:3) and UV–Vis spectra of the PDMS-PS-Ph(OH)$_2$ (7:3) coating. See DOI: https://doi.org/10.1039/d5py00442j

tions.[5] The first function involves the interaction between catechol and the adherend surfaces. Owing to their *ortho*-dihydroxy functionality, catechol components can form strong hydrogen bonds with materials featuring polar groups on their surface, such as rocks, hydroxyapatite and other substrates. Furthermore, a coordination bond can be formed, enabling adhesion to the surfaces of various metals, such as copper, aluminum and stainless steel. The second function comprises the cross-linking reaction between catechols. The cross-linking reaction leads to the formation of insoluble polydopamine *via* radical coupling or nucleophilic attack by amines. Therefore, numerous studies have been conducted on the adhesion properties of catechol components, and several catechol-functionalized organic polymers, such as poly(meth)acrylamide,[6–8] poly(meth)acrylate,[9–12] polyacrylic acid,[13] polystyrene,[14] polyvinyl alcohol,[15] polyester[16–18] and poly(ester-urea),[19] have been prepared using these components as base polymers.

In recent years, particularly in the automobile industry, multimaterial technology has gained attention as an effective approach for achieving low fuel consumption by reducing the weight of the car body structure.[20–22] In this technology, con-

ventionally used steel materials are combined with lightweight materials, such as aluminum and carbon fiber–reinforced plastic. Therefore, new joining methods that can accommodate these material changes are necessary, and adhesion-based joining is attracting attention. Because adhesive bonding is a surface technique, stress can be uniformly dispersed. Furthermore, as materials with different characteristics can be freely selected as the adhesive layer, stress can be efficiently transmitted between adherends, enhancing the strength of the entire adhering system. However, the durability of current organic polymer-based adhesives raises concerns during their long-term usage. Furthermore, temperature fluctuations result in strain between adherends possessing different thermal expansion coefficients, necessitating the use of adhesives that can relieve the stress caused by the aforementioned strain. Therefore, the adhesive should possess rigidity to maintain the strength of the entire adhering system as well as flexibility to accommodate the thermal strain due to temperature fluctuations.

Polysiloxane is useful as a base polymer, offering flexibility to address the latter issue. Because the Si–O bond in the polysiloxane main chain has a higher bond energy than the C–C bond in organic polymers, polysiloxane exhibits superior durability, heat and ultraviolet resistances and other advantages, rendering it suitable for long-term applications, such as those in the automobile industry. Moreover, because the Si–O bond distance is longer than the C–C bond distance and the Si–O–Si bond angle is larger than the C–C–C bond angle, polysiloxane possesses a flexible main chain. Therefore, it is a suitable base polymer for adhesives targeting adherends possessing different thermal expansion coefficients because it can relieve the stress resulting from thermal strain due to temperature fluctuations.

Based on the abovementioned research background, several polysiloxane-based adhesives containing catechol components have been developed.[23,24] These polymers may exhibit potential as adhesives for dissimilar adherends because they have flexible siloxane main chains. However, because the strength of pure polysiloxane is low, the lap shear strength of the aluminum plates adhered using this catechol-containing polysiloxane is 62.6 kgf cm^{-2} (~6.13 MPa) under optimal conditions.[24] Nevertheless, structural adhesives for automotive applications may require higher adhering strengths.

In this study, we aimed to develop polysiloxane-based adhesives containing catechol components to achieve the rigidity required to maintain the strength of the entire adhering system as well as the flexibility needed to accommodate the thermal strain due to temperature fluctuations. Two key steps were employed to achieve these objectives. The first step was the introduction of a catechol component into the polysiloxane main chain through a urea bond. This was expected to enhance the cohesive strength between the polymer chains *via* hydrogen bonding through the urea bonds. The second step was increasing the curing temperature during adhesion. At high temperatures, catechol-containing polysiloxane could form a cross-linked structure *via* the radical coupling of the catechol components. The aforementioned two strategies were expected to contribute to the strength of the cured adhesive.
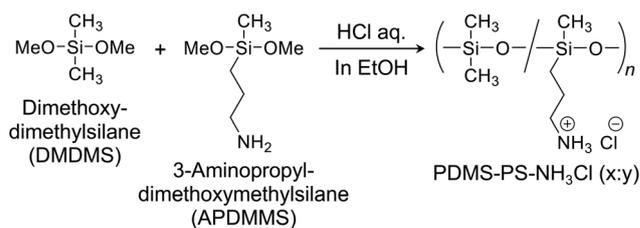
Therefore, we prepared polysiloxanes by introducing a catechol component into the side chains *via* urea bonds. Polysiloxanes containing polydimethylsiloxane (PDMS) and catechol-functionalized polysiloxane (PS-Ph(OH)$_2$) components were labelled PDMS-PS-Ph(OH)$_2$ ($x:y$), wherein "$x:y$" represents the compositional ratio of the PDMS (x) and PS-Ph (OH)$_2$ (y) components. Aluminum plates adhered using PDMS-PS-Ph(OH)$_2$ demonstrated high adhesive strength, withstanding tensile shear stresses of 12.7–21.7 MPa, and maintained strong adhesion even under impact loads. Furthermore, when a 5 kg weight was suspended from the adhered aluminum plates and the entire assembly was heated in an oven, no peeling occurred until the temperature reached 180 °C–190 °C, confirming that adhesion was maintained under high-temperature conditions. Additionally, when aluminum and stainless-steel plates, which possess different thermal expansion coefficients, were adhered using PDMS-PS-Ph(OH)$_2$ and subsequently subjected to temperature cycling between room temperature and 150 °C after suspending a weight from them, the plates did not peel off, demonstrating that PDMS-PS-Ph (OH)$_2$ could achieve effective adhesion between dissimilar materials.

Results and discussion

Preparation and characterization of PDMS-PS-NH$_3$Cl ($x:y$)

First, copolymers serving as precursors for the introduction of the catechol component were prepared. Dimethoxydimethylsilane (DMDMS) and 3-aminopropyldimethoxymethylsilane (APDMMS) were mixed in different ratios ranging from 11:1 to 5:5 (mol:mol) and stirred in ethanol at 60 °C for 12 h in the presence of catalytic amounts of HCl and purified water. These solutions were subsequently heated in an open system (~50 °C) to evaporate the solvent, and the resulting viscous solid products were further heated at 100 °C for 2 h to obtain the copolymer precursors (Scheme 1). Hereinafter, these copolymers are denoted as PDMS-PS-NH$_3$Cl ($x:y$ = 9:1–5:5) based on the approximate compositional ratio (molar ratio) of the PDMS and PS-NH$_3$Cl components in these copolymers.

When the DMDMS:APDMMS feed molar ratios were in the range of 8:2–5:5, the compositional ratio of the PDMS and

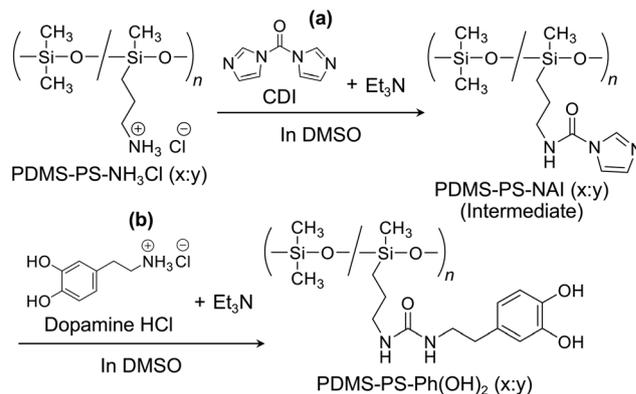
Scheme 1 Preparation of PDMS-PS-NH$_3$Cl ($x:y$).

PS-NH$_3$Cl components in the resulting copolymer closely corresponded with the feed ratio. However, when preparing a copolymer possessing a compositional ratio of 9 : 1 using the same DMDMS : APDMMS feed molar ratio, the desired compositional ratio could not be achieved. Increasing the DMDMS : APDMMS feed molar ratio to 11 : 1 successfully yielded a copolymer possessing the PDMS and PS-NH$_3$Cl components in a compositional ratio of 9 : 1. This discrepancy is considered to result from the cyclization of DMDMS during the reaction, forming low-boiling compounds that may volatilize.

In the ^{1}H nuclear magnetic resonance (NMR) spectra of PDMS-PS-NH$_3$Cl $(x : y)$, broad signals derived from the copolymers were observed. The compositional ratios of the PDMS component (x) to the PS-NH$_3$Cl component (y) in PDMS-PS-NH$_3$Cl $(8 : 2$–$5 : 5)$ closely mirrored the DMDMS : APDMM feed molar ratios (Fig. S1b–e†). However, to achieve a PDMS : PS-NH$_3$Cl compositional ratio of 9 : 1 (Fig. S1a†), the DMDMS : APDMMS feed molar ratio should be slightly increased to 11 : 1.

Additionally, to determine the average molecular weight of PDMS-PS-NH$_3$Cl $(x : y)$, the primary ammonium groups on the polymer side chains were protected through a reaction with lauroyl chloride in the presence of triethylamine (Et$_3$N) (Scheme S1†). The introduction of the lauroyl groups was confirmed via ^{1}H NMR measurements (Fig. S2†). Based on the gel permeation chromatography (GPC) measurements of the resulting products, the weight-average molecular weights (M_w) were estimated as 2.30×10^4–4.00×10^4 (molecular weight distributions ($M_w/$number-average molecular weight (M_n)): 1.32–1.76) (Fig. S3†).

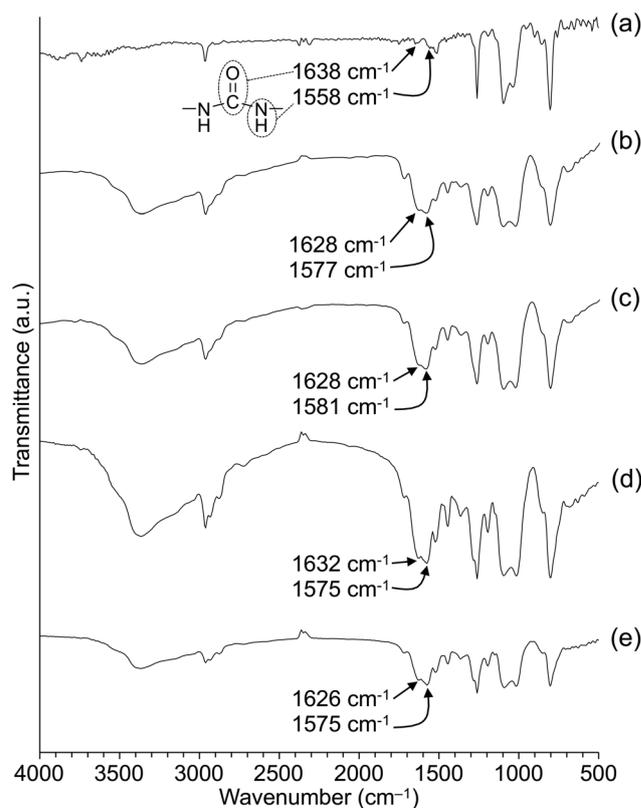### Preparation and characterization of PDMS-PS-Ph(OH)$_2$ $(x : y)$

Next, a catechol component was introduced into the PDMS-PS-NH$_3$Cl $(x : y)$ precursor to prepare catechol-containing siloxane copolymers–PDMS-PS-Ph(OH)$_2$ $(x : y)$, wherein "$x : y$" represents the compositional ratio between the PDMS component (x) and the PS-Ph(OH)$_2$ component (y). PDMS-PS-NH$_3$Cl $(8 : 2$–$5 : 5)$ and 1,1′-carbonyldiimidazole (CDI, 1.2 equivalents to the ammonium group) were mixed in dehydrated dimethyl sulfoxide (DMSO) and stirred for 15 min in the presence of Et$_3$N (1.2 equivalents to the ammonium group) to yield polysiloxane intermediates containing N-acyl imidazole groups (PDMS-PS-NAI, Scheme 2a). Without isolating the resulting intermediates, a DMSO solution comprising dopamine hydrochloride (2 equivalents to the ammonium group) and Et$_3$N (2 equivalents to the ammonium group) was added to the reaction mixture and stirred at 50 °C for 2 h (Scheme 2b). Thereafter, the reaction solution was poured into ethyl acetate, and the precipitated products were recovered and washed with water to obtain PDMS-PS-Ph(OH)$_2$ $(8 : 2$–$5 : 5)$. Furthermore, PDMS-PS-Ph(OH)$_2$ $(9 : 1)$ was prepared using a method similar to that of PDMS-PS-Ph(OH)$_2$ $(8 : 2$–$5 : 5)$; however, to address the solubility issues, the reaction solvent was changed from neat DMSO to a mixed solvent comprising DMSO and toluene. PDMS-PS-Ph(OH)$_2$ $(8 : 2$ and $7 : 3)$ were
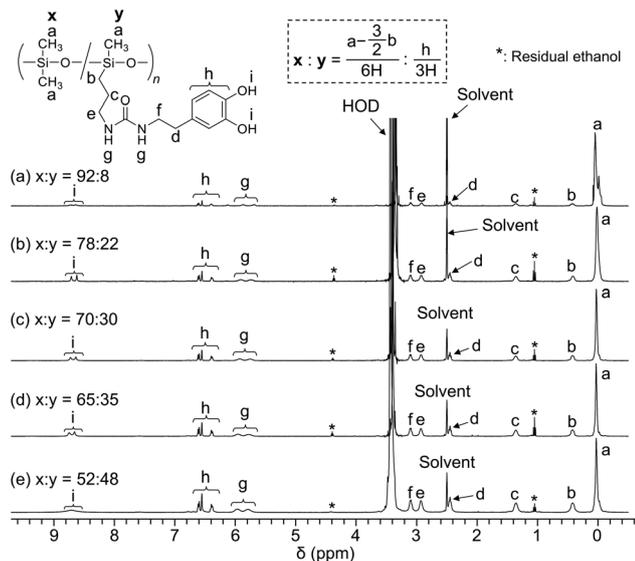
Scheme 2 Preparation of (a) PDMS-PS-NAI $(x : y)$ and (b) PDMS-PS-Ph (OH)$_2$ $(x : y)$.

obtained as paste-like solids, whereas PDMS-PS-Ph(OH)$_2$ $(6 : 4$ and $5 : 5)$ were nonpaste solids; PDMS-PS-Ph(OH)$_2$ $(9 : 1)$ was a liquid.

In the Fourier transform infrared (FT-IR) spectra of PDMS-PS-Ph(OH)$_2$ $(x : y)$, absorption peaks corresponding to the urea bond were observed at approximately 1630 and 1560 cm^{-1} (Fig. 1). Additionally, the ^{1}H NMR spectra of PDMS-PS-Ph(OH)$_2$ $(x : y)$ exhibited signals **h** attributable to the aromatic ring (Fig. 2), confirming the introduction of the cate-

Fig. 1 FT-IR spectra of PDMS-PS-Ph(OH)$_2$ $(x : y)$ in KBr pellets; $x : y$ = (a) 9 : 1, (b) 8 : 2, (c) 7 : 3, (d) 6 : 4 and (e) 5 : 5.
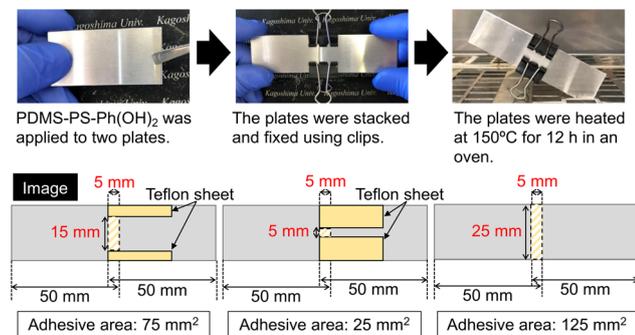
Fig. 2 ^{1}H NMR spectra in DMSO-d_6 of PDMS-PS-Ph(OH)$_2$ (x : y); x : y = (a) 9 : 1, (b) 8 : 2, (c) 7 : 3, (d) 6 : 4 and (e) 5 : 5. Chemical shifts are referenced to DMSO-d_6 (δ 2.5).

chol component *via* covalent bonds. Furthermore, the compositional ratios of the PDMS component (x) to the PS-Ph(OH)$_2$ component (y), calculated using the integral ratio of the signals **a** of the methyl protons adjacent to the silicon atom and the signals **h** of the aromatic ring, were approximately equivalent to those of the PDMS-PS-NH$_3$Cl (x : y) precursors.

Method of adhesion between the two plates

PDMS-PS-Ph(OH)$_2$ (x : y) was applied to two plates (aluminum or stainless steel) heated using a hot plate (~50 °C). The plates were stacked, fixed using clips, and heated at 150 °C for 12 h in an oven (Fig. 3). After cooling to room temperature (~25 °C), the clips were removed, and the samples were used for evaluating adhesiveness. Adhesion was assessed using a tensile shear test, and the adhesive area was adjusted to 75 mm^2 (5 × 15 mm). For the samples exhibiting strong adhesion (*i.e.*, no peeling off even under the maximum load of 1020 N), the adhesive area was reduced to 25 mm^2 (5 × 5 mm). To evaluate
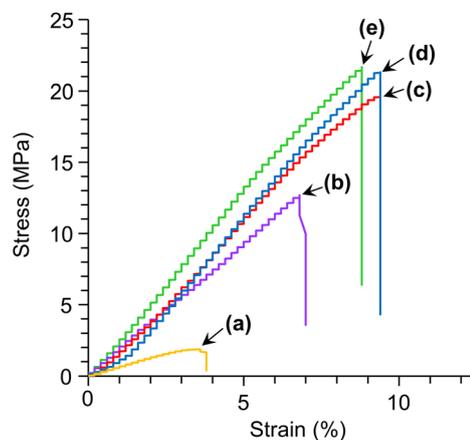

Fig. 3 Method of adhesion between the adherends (*e.g.*, aluminum plates) using PDMS-PS-Ph(OH)$_2$ (x : y).

the adhesive properties under the conditions of impact loads and high temperatures, the adhesive area was set to 125 mm^2 (5 × 25 mm).

Evaluation of adhesiveness using the tensile shear test

The adhesiveness of the aluminum plates adhered using PDMS-PS-Ph(OH)$_2$ (x : y) was evaluated *via* tensile shear tests at room temperature. PDMS-PS-Ph(OH)$_2$ (9 : 1) (Fig. 4a), which contains a higher proportion of the PDMS component, exhibited a lower tensile shear stress (1.87 MPa; adhesive area: 75 mm^2). In contrast, the tensile shear stresses required to peel off the aluminum plates were 12.7, 19.6, 21.3 and 21.7 MPa for PDMS-PS-Ph(OH)$_2$ (8 : 2) (Fig. 4b), PDMS-PS-Ph(OH)$_2$ (7 : 3) (Fig. 4c), PDMS-PS-Ph(OH)$_2$ (6 : 4) (Fig. 4d) and PDMS-PS-Ph(OH)$_2$ (5 : 5) (Fig. 4e), respectively, as summarized in Table 1. These findings suggest that a compositional ratio comprising >20% of the PS-Ph(OH)$_2$ component is crucial for achieving a high tensile shear stress (>10 MPa).

Their failure modes were predominantly identified as cohesive fractures based on visual observation. In this assessment, aluminum plates adhered using PDMS-PS-Ph(OH)$_2$ (7 : 3) were

Fig. 4 Stress–strain curves obtained *via* the tensile shear tests of the aluminum plates adhered using PDMS-PS-Ph(OH)$_2$ (x : y); x : y = (a) 9 : 1, (b) 8 : 2, (c) 7 : 3, (d) 6 : 4 and (e) 5 : 5.

Table 1 Summary of monomer feed ratios, ^{1}H NMR-determined compositional ratios and tensile shear stresses required to peel off the aluminum plates adhered with PDMS-PS-Ph(OH)$_2$ (x : y)

Run	PDMS-PS-Ph(OH)$_2$		Fracture stress^c (MPa)
	$(x:y)^a$	$(x:y)^b$	
1	9 : 1	92 : 8	1.87
2	8 : 2	78 : 22	12.7
3	7 : 3	70 : 30	19.6
4	6 : 4	65 : 35	21.3
5	5 : 5	52 : 48	21.7

^{a} Feed ratio of DMDMS to APDMMS. ^{b} Compositional ratios of PDMS to PS-Ph(OH)$_2$ components estimated by ^{1}H NMR analysis. ^{c} Evaluated by tensile shear test.

selected as a representative example (Fig. S4†). Furthermore, scanning electron microscopy (SEM) images revealed adhesive residue remaining on the fractured surfaces of the aluminum plates (Fig. S5†), providing additional support for the occurrence of cohesive fracture. Energy-dispersive X-ray spectroscopy (EDX) detected silicon atoms at spots 1–3 on the fractured surfaces in the SEM image shown in Fig. S5 (Table S1†), offering further evidence of cohesive failure. These SEM and EDX results collectively confirm that the failure mode was cohesive in nature.

For comparison, tensile shear tests were performed using the PDMS-PS-NH$_3$Cl ($x : y$) precursor copolymers. The tensile shear stresses required for peeling off the plates were 0.79, 1.49, 4.09, 2.95 and 2.37 MPa for PDMS-PS-NH$_3$Cl (9 : 1) (Fig. S6a†), PDMS-PS-NH$_3$Cl (8 : 2) (Fig. S6b†), PDMS-PS-NH$_3$Cl (7 : 3) (Fig. S6c†), PDMS-PS-NH$_3$Cl (6 : 4) (Fig. S6d†) and PDMS-PS-NH$_3$Cl (5 : 5) (Fig. S6e†), respectively. All these values were lower than those obtained for PDMS-PS-Ph(OH)$_2$ ($x : y$). These results demonstrate that the catechol component in the side chains of PDMS-PS-Ph(OH)$_2$ ($x : y$) plays a crucial role in enhancing adhesion.

Evaluation of adhesiveness under impact loads

The adhesiveness of the aluminum plates adhered using PDMS-PS-Ph(OH)$_2$ (8 : 2–5 : 5) (adhesive area: 125 mm^2), which demonstrated strong adhesion in the aforementioned tensile shear tests, was evaluated under impact loads. The plates were subjected to hammer strikes perpendicular to the adhesive surface (Fig. 5). When peeling off did not occur, the plates

were flipped to strike the opposite side, and this procedure was repeated up to five times. The aluminum plates adhered using PDMS-PS-Ph(OH)$_2$ (8 : 2 and 7 : 3) did not peel off; instead, they underwent deformation (Fig. 5a and b), indicating the strong resistance to impact loads. Conversely, the aluminum plates adhered using PDMS-PS-Ph(OH)$_2$ (6 : 4 and 5 : 5) occasionally remained adhered after the first impact; however, most of them peeled off upon subsequent strikes (Fig. 5c and d). The plates adhered using PDMS-PS-Ph(OH)$_2$ (8 : 2 and 7 : 3) remained adhered even after repeated hammer strikes. These results suggest that PDMS-PS-Ph(OH)$_2$ (6 : 4 and 5 : 5) have a lower impact resistance than PDMS-PS-Ph(OH)$_2$ (8 : 2 and 7 : 3).

The aforementioned results emphasize the importance of the flexible PDMS component for the impact load resistance of PDMS-PS-Ph(OH)$_2$ ($x : y$). This is plausibly because of the mitigation of the stress due to the impact-induced strain by the PDMS component. However, the plates adhered using PDMS-PS-Ph(OH)$_2$ (9 : 1) peeled off upon the first impact, indicating that an excess of the PDMS component reduces the adhesive strength under impact loads. These findings indicate that the balance between the PDMS and PS-Ph(OH)$_2$ components plays a critical role in determining the mechanical performance of the adhesives, particularly in achieving flexibility provided by the PDMS component and sufficient cohesive and adhesive strength contributed by the PS-Ph(OH)$_2$ component. Therefore, these results clearly demonstrate that an optimal compositional ratio of the PDMS and PS-Ph(OH)$_2$ components is crucial for achieving a high adhesive performance in both the tensile shear test and impact load test.

Adhesive properties at high temperatures

To investigate the adhesive properties at high temperatures, a 5 kg weight was suspended from the aluminum plates adhered using PDMS-PS-Ph(OH)$_2$ (8 : 2 and 7 : 3), which demonstrated strong adhesion in both the aforementioned tensile shear test and impact load test. The adhered aluminum plates were subsequently heated in an oven. For PDMS-PS-Ph(OH)$_2$ (8 : 2), the weight remained adhered up to 180 °C; however, it was dropped and the plates peeled off at 190 °C (Fig. 6a). Conversely, for PDMS-PS-Ph(OH)$_2$ (7 : 3), the weight did not drop at 190 °C, and adhesion was maintained until peeling occurred at 200 °C (Fig. 6b).

To evaluate the thermal stability of the cured material, thermogravimetric analysis (TGA) was performed on the PDMS-PS-Ph(OH)$_2$ (7 : 3) sample after heat treatment at 150 °C for 12 h. The cured material exhibited an initial decomposition temperature of 218 °C and a 10% weight loss temperature (T_{d10}) of 293 °C (Fig. S7†). Accordingly, the adhesive failure observed at 200 °C is likely attributable to the onset of thermal degradation, as indicated by the TGA results.

Although PDMS-PS-Ph(OH)$_2$ (8 : 2 and 7 : 3) were polymers composed of flexible siloxane main chains, they retained their adhesive properties at relatively high temperatures (180 °C–190 °C). This could be attributed to the radical coupling reaction between the catechol components in PDMS-PS-Ph(OH)$_2$
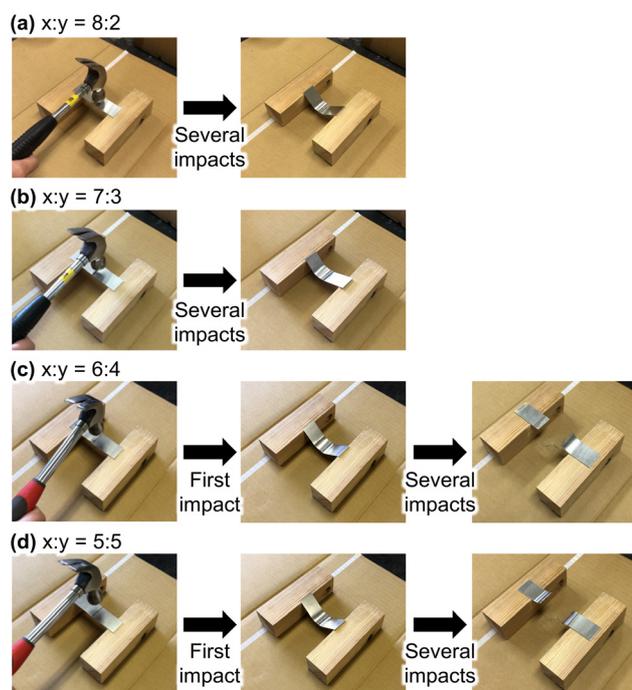

Fig. 5 Evaluation of adhesiveness under impact loads for the aluminum plates adhered using PDMS–PS-Ph(OH)$_2$ ($x : y$); $x : y$ = (a) 8 : 2, (b) 7 : 3, (c) 6 : 4 and (d) 5 : 5.
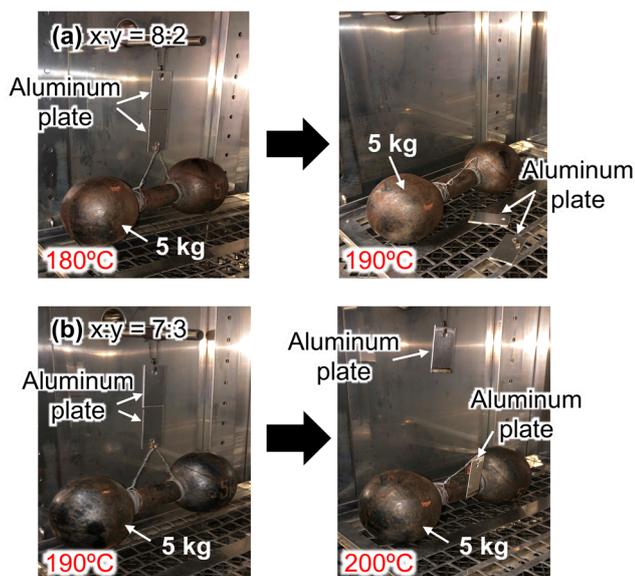
Fig. 6 Evaluation of adhesiveness at high temperatures for the aluminum plates adhered using PDMS-PS-Ph(OH)$_2$ ($x:y$); $x:y$ = (a) 8:2 and (b) 7:3.

Fig. 7 Evaluation of adhesiveness at high temperatures (150 °C) between the aluminum and stainless-steel plates adhered using PDMS-PS-Ph(OH)$_2$ ($x:y$); $x:y$ = (a) 8:2 and (b) 7:3.

(8:2 and 7:3) upon heating, which formed a network (cross-linked) structure. To investigate structural changes associated with reactions between catechol groups, ultraviolet–visible (UV–Vis) absorption spectroscopy was performed on coatings prepared by applying the precursor (*e.g.*, PDMS-PS-Ph(OH)$_2$ (7:3)) to a glass plate and heating it at 150 °C for 12 h. Before heating, the coating was colorless and transparent, with almost no absorption observed above 310 nm (Fig. S8a†). After heating, however, the coating turned yellow-brown and exhibited a red shift in the absorption edge, extending to ~500 nm (Fig. S8b†). This change in absorption characteristics suggests an extension of the π-conjugated system due to reactions involving catechol groups, supporting the occurrence of inter- or intramolecular coupling reactions during heat treatment. These findings indicate the formation of a network (cross-linked) structure. Consequently, softening—which would considerably reduce adhesion—was prevented even at high temperatures.

Adhesive properties for dissimilar materials

The adhesive properties of PDMS-PS-Ph(OH)$_2$ (8:2 and 7:3) were evaluated using aluminum and stainless-steel plates (linear coefficients of expansion: ~2.28 × 10^{-5} K^{-1} and ~1.04 × 10^{-5}–1.73 × 10^{-5} K^{-1}, respectively) as dissimilar materials possessing different thermal expansion coefficients. The plates were adhered using the same method as that used for the aluminum plates, with an adhesive area of 125 mm^2. Adhesion was assessed by suspending a 5 kg weight from the adhered plates, followed by heating the system to 150 °C in an oven and subsequently cooling it to room temperature. Adhesion was evaluated by monitoring whether the plates remained adhered after cooling.
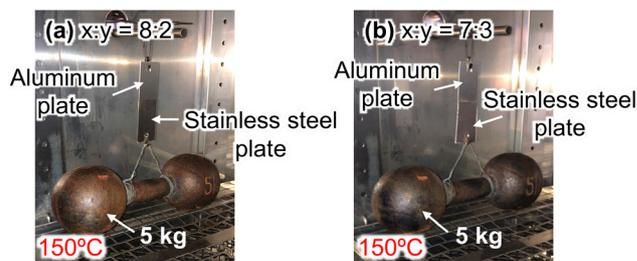
For both PDMS-PS-Ph(OH)$_2$ (8:2 and 7:3), the weights did not drop when heated to 150 °C (Fig. 7), and adhesion was maintained upon returning to room temperature. This was plausibly because of the flexible PDMS component, which alleviated the stress caused by the thermal strain resulting from the difference in the thermal expansion coefficients of aluminum and stainless steel. Indeed, differential scanning calorimetry (DSC) of the cured PDMS-PS-Ph(OH)$_2$ (7:3) sample (heat-treated at 150 °C for 12 h) revealed a glass transition temperature (T_g) of 45 °C (Fig. S9†), suggesting that the cured material exhibits rubbery behavior at temperatures above T_g. Furthermore, the formation of a cross-linked structure through the radical coupling reaction between the catechol components prevented flow at high temperatures, ensuring stable adhesion.

Conclusions

In this study, aluminum plates were adhered using copolymers possessing different PDMS:PS-Ph(OH)$_2$ component ratios, ranging from 9:1 to 5:5 (PDMS-PS-Ph(OH)$_2$ (9:1–5:5)). The adhesive properties were evaluated through room-temperature tensile shear tests. PDMS-PS-Ph(OH)$_2$ (8:2–5:5) exhibited strong adhesion (12.7–21.7 MPa), whereas PDMS-PS-Ph(OH)$_2$ (9:1) offered weaker adhesion (1.87 MPa) because of its lower catechol (PS-Ph(OH)$_2$) content. Since few conventional catechol-containing polymer adhesives have demonstrated tensile shear strengths exceeding 10 MPa, the PDMS-PS-Ph(OH)$_2$ copolymers developed in this study (excluding the 9:1 composition) outperformed most previously reported catechol-based adhesives.

Impact load tests were performed on the aluminum plates adhered using PDMS-PS-Ph(OH)$_2$ (8:2 and 7:3), and peeling off was not observed even after multiple hammer impacts. However, the aluminum plates adhered using PDMS-PS-Ph(OH)$_2$ (6:4 and 5:5) peeled off after multiple hammer strikes, suggesting that an excessive PS-Ph(OH)$_2$ component would lead to brittleness and a reduced impact resistance. These results demonstrate that the balance between the PDMS and PS-Ph(OH)$_2$ components is critical for achieving both flexibility and mechanical strength, particularly flexibility from the

PDMS component and cohesive and adhesive strength from the PS-Ph(OH)$_2$ component.

Furthermore, when a 5 kg weight was suspended from the aluminum plates adhered using PDMS-PS-Ph(OH)$_2$ (8 : 2 and 7 : 3) and the system was subsequently heated in an oven, the plates maintained adhesion up to 180 °C and 190 °C, respectively, without peeling off, indicating adhesive stability at high temperatures. This thermal stability is attributed to the formation of cross-linked structures through radical coupling between the catechol components during heating.

Additionally, PDMS-PS-Ph(OH)$_2$ (8 : 2 and 7 : 3) were used to adhere plates possessing different thermal expansion coefficients, such as aluminum and stainless-steel plates. When a 5 kg weight was suspended from the adhered plates and the temperature was cycled between room temperature and 150 °C, no peeling off was observed. This suggests that PDMS-PS-Ph(OH)$_2$ (8 : 2 and 7 : 3) are effective for adhering dissimilar materials. The formation of cross-linked structures through radical coupling between the catechol components maintains adhesion at high temperatures, whereas the flexibility of polysiloxane plausibly alleviates the stress caused by the temperature-induced thermal expansion.

Future research will focus on the application of catechol-functionalized siloxane polymers for the adhesion of dissimilar materials, particularly those with considerably different thermal expansion coefficients, such as resins and metals. This approach aims to accelerate the practical implementation of multimaterial bonding using adhesives and broaden its applications across various industrial fields.

Author contributions

AF, SO, YS and YU prepared and analyzed compounds. AF and SO wrote the draft manuscript. TA and TO evaluated the adhesion. HN and YK devised a concept and synthesis strategy. YK wrote and edited the manuscript. All authors discussed the results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the ESI.†

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References

1 H. Lee, N. F. Scherer and P. B. Messersmith, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 12999–13003.

2 R. J. Stewart, T. C. Ransom and V. Hlady, *J. Polym. Sci., Part B:Polym. Phys*, 2011, **49**, 757–771.

3 J. Yu, W. Wei, E. Danner, R. K. Ashley, J. N. Israelachvili and J. H. Waite, *Nat. Chem. Biol.*, 2011, **7**, 588–590.

4 A. Hagenau, M. H. Suhre and T. R. Scheibel, *Prog. Polym. Sci.*, 2014, **39**, 1564–1583.

5 N. Patil, C. Jérôme and C. Detrembleur, *Prog. Polym. Sci.*, 2018, **82**, 34–91.

6 B. J. Sparks, E. F. T. Hoff, L. P. Hayes and D. L. Patton, *Chem. Mater.*, 2012, **24**, 3633–3642.

7 Y. Saito, T. Kawano, M. Shimomura and H. Yabu, *Macromol. Rapid Commun.*, 2013, **34**, 630–634.

8 J. Nishida, M. Kobayashi and A. Takahara, *ACS Macro Lett.*, 2013, **2**, 112–115.

9 H. Lee, B. P. Lee and P. B. Messersmith, *Nature*, 2007, **448**, 338–341.

10 S. B. Lee, C. González-Cabezas, K. M. Kim, K. N. Kim and K. Kuroda, *Biomacromolecules*, 2015, **16**, 2265–2275.

11 B. D. B. Tiu, P. Delparastan, M. R. Ney, M. Gerst and P. B. Messersmith, *ACS Appl. Mater. Interfaces*, 2019, **11**, 28296–28306.

12 Y. Zhang, K. Hasegawa, S. Kamo, K. Takagi, W. Ma and A. Takahara, *ACS Appl. Polym. Mater.*, 2020, **2**, 1500–1507.

13 T. Harper, R. Slegeris, I. Pramudya and H. Chung, *ACS Appl. Mater. Interfaces*, 2017, **9**, 1830–1839.

14 M. A. North, C. A. D. Grosso and J. J. Wilker, *ACS Appl. Mater. Interfaces*, 2017, **9**, 7866–7872.

15 Y. Mu and X. Wan, *Macromol. Rapid Commun.*, 2016, **37**, 545–550.

16 C. L. Jenkins, H. M. Siebert and J. J. Wilker, *Macromolecules*, 2017, **50**, 561–568.

17 Y. Xu, Q. Liu, A. Narayanan, D. Jain, A. Dhinojwala and A. Joy, *Adv. Mater. Interfaces*, 2017, **4**, 1700506.

18 H. M. Siebert and J. J. Wilker, *ACS Sustainable Chem. Eng.*, 2019, **7**, 13315–13323.

19 J. Zhou, A. P. Defante, F. Lin, Y. Xu, J. Yu, Y. Gao, E. Childers, A. Dhinojwala and M. L. Becker, *Biomacromolecules*, 2015, **16**, 266–274.

20 X. Cui, S. Wang and J. Hu, *Mater. Des.*, 2008, **29**, 381–387.

21 M. D. Banea, M. Rosioara, R. J. C. Carbas and L. F. M. da Silva, *Compos. B. Eng*, 2018, **151**, 71–77.

22 J. J. M. Machado, P. D. P. Nunes, E. A. S. Marques and L. F. M. da Silva, *Compos. B. Eng*, 2019, **158**, 102–116.

23 J. Heo, T. Kang, S. G. Jang, D. S. Hwang, J. M. Spruell, K. L. Killops, J. H. Waite and C. J. Hawker, *J. Am. Chem. Soc.*, 2012, **134**, 20139–20145.

24 J. Moon, Y. Huh, J. Park, H. W. Kim, Y. Choe, J. Huh and J. Bang, *ACS Appl. Polym. Mater.*, 2020, **2**, 2444–2451.