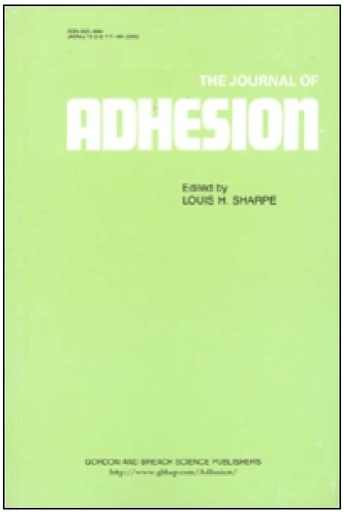

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Adhesion of PDMS Elastomers to Functional Substrates

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Adhesion of PDMS Elastomers to Functional Substrates

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The JKR technique was applied to study the influence of interfacial reactions on the adhesion between functional elastomer gels and functional solid substrates. The gelation chemistry of poly(dimethyl siloxane) (PDMS) gels cured by hydrosilylation reactions was purposely adjusted to produce an excess of either silane or vinyl functionality. Hemispherical lenses of these materials were then contacted under load with a variety of functionalized solid substrates: poly(styrene-b-butadiene) copolymers with vinyl functionality, vinyl-terminated trimethoxysilane self-assembled monolayers, and α,ω*-functional PDMS brushes terminated with either monomethoxy or hydroxyl groups. To rule out chain interpenetration effects, the molecular weights were kept below the entanglement molecular weight or immiscible polymers were employed on opposite sides of the interface. Significant adhesion enhancement was observed for most systems, indicating that a variety of different interfacial reactions can occur across the interface between PDMS elastomers and solid polymeric substrates. The overall nature of the adhesion enhancement found is consistent with the predictions of the Lake–Thomas theory for failure of elastomers, increasing linearly with the length and areal density of covalent linker chains that span the interface.*

Keywords: Elastomer adhesion; JKR; Lake–Thomas model; PDMS

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INTRODUCTION

The so-called JKR method, popularized by Chaudhury and Whitesides [1–3], has become an important tool for the investigation of adhesion between solids, particularly for elastomeric-polymer systems. The method is based on an extension of Hertzian contact theory [4] and is named after its developers, Johnson, Kendall, and Roberts [5]. The model quantitatively accounts for the fact that adhesive forces between a soft elastomeric sphere and a substrate produce a contact area that is larger than that predicted by Hertz analysis.

Many of the initial studies of adhesion in elastomers applied the JKR method to examine how a glassy substrate could be modified to enhance its adhesion toward an elastomer. Of particular interest have been the effects of tethering various rubbery polymer chains to the substrate, either by addition of an appropriate block copolymer [6–10], by the adsorption of “Guiselein” brushes [11–13] or by grafting end-tethered brushes [14–15]. A number of so-called chain-pullout models were developed to predict the adhesion enhancement afforded by substrate modification with polymer chains [15–22] and have been compared with experimental results for several elastomer systems. The basic predictions of chain-pullout theories have, for the most part, been borne out in experiments: the fracture toughness increases essentially linearly with molecular weight of the brush and shows a maximum as a function of the areal brush density, increasing first as a result of interpenetration between the elastomer gel and brush but falling back to the thermodynamic work of adhesion as the brush density becomes too high to allow for significant penetration into the elastomer gel.

The adhesion behavior of poly(dimethyl siloxane) elastomers has been widely studied because they have a very flexible chemistry that allows them to be fabricated from functional macromonomer precursors to produce a wide range of physical and mechanical properties. Careful experiments on PDMS elastomers have shown that chain-interpenetration effects for these systems develop very slowly over a period of months or even longer [14]. Significant adhesion effects for modified elastomer interfaces, however, have often been seen for even short contact times. Hysteresis, for example, has frequently been observed in loading and unloading curves for PDMS elastomers that have been in contact with a substrate for only minutes [23–29]. We have recently shown that much of this behavior can be attributed to the occurrence of interfacial reactions between the PDMS elastomer and the modified substrate [30].

The goal of this article is to further probe the effects of interfacial reactions on the adhesion behavior of PDMS elastomers by applying the JKR method to measure the fracture toughness of functional PDMS elastomers in contact with substrates functionalized with a number of chemical groups that are capable of reactions with silicone elastomers. The results show clearly that a wide variety of chemical reactions can occur between PDMS elastomers and functional surfaces, causing significant enhancement in the interfacial fracture toughness measured by the JKR technique.

EXPERIMENTAL

Materials

Two poly(styrene-b-butadiene) block copolymers P(S-b-B) were synthesized by Adel Halasa from the Goodyear Tire and Rubber Company using anionic polymerization with n-butyl lithium as the initiator. A "monodisperse" block copolymer was prepared by terminating the reaction with excess methanol, and a "polydisperse" copolymer containing a polybutadiene (PB) block of increased polydispersity, but the same number average molecular weight, was prepared by the addition of small amounts of a chlorosilane during the butadiene polymerization to selectively terminate 10% of chain ends at a time. The characteristics of the block copolymers [31] were determined by gel-permeation chromatography (Waters 150-C, Waters, Milford, MA, USA), ultraviolet-visible (UV-Vis) spectroscopy (Perkin Elmer Lambda 6, Perkin Elmer, Shelton, CT, USA), and ^{1}H nuclear magnetic resonance (^{1}H NMR) spectroscopy measurements (Bruker DMX-500, Bruker, Billerica, MA, USA) and are reported in Table 1.

Substrates

Four types of functional substrates were examined [31]. Bare silicon wafers with reactive-surface silanol groups were used, as well as

TABLE 1 Characteristics of P(S-b-B) Block Copolymers

Sample designation	Mn total (kDalton-GPC)	Mw/Mn (GPC)	(UV-Vis) wt.% PS	Mn PB (kDalton)	Vinyl in PB (^{1}H-NMR) (Mol%)
PSPB93M (monodisperse)	172.1	1.25	45.9	93.1	12.1
PSPB91P (polydisperse)	173.1	1.33	47.4	91.1	14.4

silicon wafers coated with three different types of organic materials: a vinyl-functional block copolymer, a vinyl-functional silane self-assembled monolayer (SAM), and tethered α,ω-functional PDMS brushes.

P(S-b-B) block copolymers were spin-coated onto silicon wafers that were precoated with a 25-nm-thick end-tethered polystyrene brush layer of trimethoxysilane-terminated PS (PS-Si[OCH_3]$_3$) (Scientific Polymer Products, Inc., Ontario, NY, USA: $M_n = 209{,}000\,\mathrm{g/mol}$, $M_w = 226{,}000\,\mathrm{g/mol}$). The PS block spontaneously entangles with the tethered PS substrate, whereas the PB blocks self-assemble to create a vinyl-functional surface layer. The areal chain density of block copolymers, Σ, was calculated from the film thickness by the following formula:

$$\Sigma = \frac{t\rho N_a}{M} \tag{1}$$

where N_a is Avogadro's number and t, ρ, and M are the block-copolymer film thickness, density, and molecular weight, respectively.

A second type of vinyl-functionalized surface was prepared by self-assembly of a vinyldimethylchlorosilane (Gelest, Inc., Morrisville, PA, USA) monolayer onto a clean silicon wafer from hexane according to the procedure used by Reiter and Khanna [32].

α,ω-Monomethoxy-terminated PDMS ($M_n = 1000\,\mathrm{g/mol}$, 3.2 nm thick) and α,ω-hydroxy-terminated PDMS (4,200; 26,000; 49,000; and 110,000 g/mol) were coated onto the wafers, annealed to promote anchoring, and rinsed to remove untethered PDMS.

Film thickness was determined by ellipsometry (J.A. Woolam, Lincoln, NE, USA). Examination by optical microscopy and AFM (TMX 2000 Explorer) showed that the substrates employed were smooth and homogeneous with no unusual features. A Physical Electronics (Eden Priarie, MN, USA) PHI 5300 XPS system equipped with an aluminum Kα X-ray source (1487.6 eV, line width 0.85 eV), a monochromator, a hemispherical analyzer, and multichannel detector was used to analyze sample surface composition.

Elastomer Lenses

PDMS elastomer lenses required for the JKR experiments were synthesized *via* an additional cure reaction wherein cross-links are formed by hydrosilylation reactions between silane (SiH) and vinyl groups in the presence of platinum catalyst. The method used was based on a number of similar procedures published in the literature [1, 11, 12, 30, 31, 33, 34]. Two families of cross-linked PDMS lenses were synthesized from α,ω-functional macromonomers terminated

TABLE 2 Characteristics of α,ω-Vinyl-Terminated PDMS Macromonomers

Code	Viscosity	Molecular weight	Vinyl (wt.%)
DMS-V21	100	6,000	0.8–1.2
DMS-V22	200	9,400	0.4–0.6
DMS-V25	500	17,200	0.37
DMS-V31	1000	28,000	0.18
DMS-V33	3500	43,000	0.12
DMS-V41	10,000	62,700	0.08
DMS-V42	20,000	72,000	0.07

with either vinyl or hydride functional groups. Vinyl-terminated PDMS macromonomers (Table 2) were cross-linked by addition of a poly(methylhydrosiloxane-dimethylsiloxane) copolymer [P(MHS-co-DMS)] (1950 g/mol, 25–30% MHS). Hydride-terminated PDMS macromonomers (Table 3) were cross-linked by addition of a poly (vinylmethylsiloxane-dimethylsiloxane) copolymer [P(VMS-co-DMS)] (26,500 g/mol, 7.5% vinyl). Chemical structures for the gel precursors are shown in Figure 1.

A platinum-divinyltetramethyldisiloxane complex in xylene (2.1–2.4% Pt, room-temperature catalyst) and a platinum-cyclovinylmethyl complex in xylene (3–3.5% Pt, low-temperature catalyst) were used to catalyze the hydrosilylation cure reactions for both systems. All materials were purchased from Gelest, Inc. and used as received.

The sample designations of the PDMS lenses employed first denote the molecular weight (*e.g.*, 6 K for 6,000 Dalton) of the PDMS macromonomer employed (either divinyl terminated or dihydride terminated). The type of cross-linker used is next denoted by which functional group is expected to be in excess. When the crosslinker is P(MHS-co-DMS), SiH groups will be in excess (denoted as SiH), whereas vinyl groups are in excess (denoted as vinyl) when the cross-linker is P(VMS-co-DMS). The next part of the designation code indicates the ratio of the cross-linker to the macromonomer. For example, the code R13 indicates ratios of 1.3 mol of SiH to 1 mol of vinyl for lenses cured with P(MHS-co-DMS) or 1.3 mol of vinyl to

TABLE 3 Characteristics of α,ω-Hydride-Terminated PDMS Macromonomers

Code	Viscosity	Molecular weight	Hydride %
DMS-H21	100	6000	0.04
DMS-H31	1000	28,000	0.007

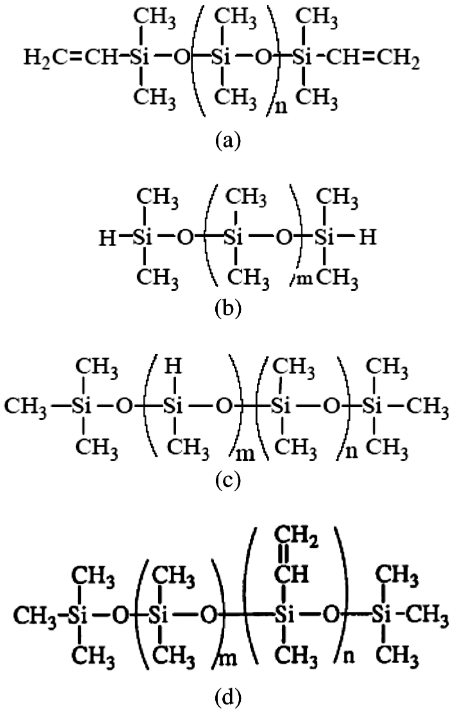


FIGURE 1 Chemical structures of PDMS gel precursors: a) vinyl-terminated PDMS macromonomer, b) hydride-terminated PDMS macromonomer, c) poly(hydromethyl-co-dimethyl siloxane) crosslinker, d) poly(vinylmethyl-co- dimethyl siloxane) crosslinker.

1 mol of SiH for P(VMS-co-DMS) cured lenses. The designation PDMS43KR13SiH, therefore, refers to a lens prepared from a 43,000-Dalton divinyl PDMS macromonomer, cured with P(MHS-co-DMS) with a SiH-to-vinyl ratio of 1.3.

The off-stoichiometric reactant ratios employed provide either excess vinyl functionality or excess silane functionality in the lenses. Dangling chains are avoided by incorporating the excess functional groups on the copolymer cross-linkers, so that the reaction of the end-functional macromonomers can be driven to completion.

Small hemispherical droplets (*i.e.*, lenses) between 0.5 and 2 mm in diameter were created by depositing the elastomers onto hydrophobically modified glass slides that were prepared by immersing clean glass slides into a solution of (tridecafluoro-1,1,2,2-tetrahydrooctyl) 1-trichlorosilane in hexane (~1 wt.%) for approximately 1 min. The lenses gelled after about 4 h at room temperature with the low-temperature catalyst, but to ensure complete reaction, the hemispheres were transferred to a vacuum oven and heated to 65°C for at least 2 h. Sol fractions were removed from all lenses by extraction in toluene and were determined by measuring the weight of the lenses before and after extraction.

One half of the lenses, designated as "poisoned," were treated with a thiol solution to poison the residual platinum catalyst and inhibit subsequent hydrosilylation reactions. 1-Dodecanethiol (1 wt.%) was added for this purpose to the first toluene wash for lenses designated for poisoning.

The silane and vinyl functionalities of the PDMS macromonomers and cured lenses were characterized using Fourier transform infrared spectroscopy (Nicolet Magna 560, Nicolet, now part of Thermo Electron, Madison, WI, USA) in the attenuated total reflectance mode (ATR-FTIR) and Raman spectroscopy (Renishaw 2000, Renishaw, New Mills, Gloucestershire, UK) [31]. The functionality of post-cure lenses was analyzed by curing a flat film, from the same mixture as the lens, onto a fluorosilane-treated glass slide. ATR-FTIR spectra were collected by contacting the film against a (KRS5) crystal.

Lens Modulus and Adhesion Measurements

The moduli of the lenses and their adhesion toward various substrates were determined by application of the JKR method. First, the lens modulus was determined by measurement of the load dependence of contact area for PDMS lenses in contact with silicon substrates that were coated with a monolayer of end-tethered PS ($PS\text{-}Si[OCH_3]_3$). The loading curve was obtained by progressively stacking small rectangles cut from laser transparencies until a maximum load of 0.5 g was applied to the lens. Each rectangle was 25 mm × 20 mm and weighed approximately 0.065 g. The unloading curve was obtained by progressive removal of the rectangles. Loading and unloading were performed in a stepwise manner with a dwell time of 5 min between each step. A two-parameter fit to Equation (2) provided estimates of the modulus, K, and work of adhesion, W_a, for a given load, P, and lens radius of curvature, R [5, 35]:

$$a^3 = \frac{R}{K}\left[P + 3W_a\pi R + \sqrt{(6W_a\pi RP + [3W_a\pi R]^2)}\right]. \tag{2}$$

Images of the contact area were recorded with a Nikon Metaphot optical microscope (Nikon, Melville, NY, USA) equipped with a Sony

CCD camera (Sony, New York, NY, USA) and attached to a PC system. The 5× objective was used yielding an overall magnification of 63×. The contact diameter was obtained by calibrating with a 1 mm graticule taken at the same magnification as the sample. After each JKR experiment, the lens was weighed and an image of its profile was analyzed to determine the radius of curvature. Side-view images were taken using an apparatus designed for sessile drop contact-angle measurements. This comprised a CCD camera connected to a variable-focus zoom lens attached to a computer with a frame grabber to capture the image.

The work of adhesion for each lens–substrate combination was determined by crack-growth measurements using the JKR technique. A Plexiglas® sample holder was used to align the lens and substrate with an applied load, the latter consisting of a glass slide or a cover slip, 40 mm × 25 mm in size. After a typical dwell time of 24 h, the entire load was rapidly removed, and the contact radius monitored as function of time. Typically, measurements were performed over periods of time that ranged from a few days to several weeks, until there was no more discernable change in the contact radius. The contact radius was measured by analysis (Scion Image® software from Scion Corporation, Frederick, MD, USA) of digital images recorded by optical microscopy using a 10× objective. The fracture toughness at any time, $G(t)$, was calculated from the modulus measured for the lens, the initial applied load, P, and the contact radius, $a(t)$, by applying the relation [5]:

$$G(t) = \frac{1}{6\pi K\{a(t)\}^3}\left[\frac{K\{a(t)\}^3}{R} - P\right]^2. \tag{3}$$

The crack velocity was calculated from a point-by-point fit of the contact radius, a, *versus* time, t, curve. Experimental $G(t)$ data generally show two more or less linear regimes of behavior. The zero-rate fracture energy or threshold toughness, G_0, was generally obtained by linear extrapolation of the lower rate $G(t)$ data (typically below 1 nm/s) to zero time, as has been done in previous work [7, 33, 34].

RESULTS AND DISCUSSION

Characterization of Elastomeric PDMS Lenses

The goal of this research was to investigate the role of interfacial reactions in enhancing the adhesion of PDMS elastomers. For this purpose, elastomeric lenses with residual silane or vinyl groups were placed in contact with a variety of different reactive functional substrates to measure the interfacial fracture toughness by the JKR technique. Two cases were examined: "nonpoisoned" lenses that contained residual active platinum catalyst and "poisoned" lenses to which thiols were added to inactivate any residual platinum catalyst.

The first task was to prepare and characterize PDMS elastomeric lenses with residual reactive chemical functionality. The mechanical integrity of the off-stoichiometric lenses was assured by incorporating excess reactant groups along copolymer cross-linker chains and limiting reactant groups on the end-functional macromonomers. In this fashion, dangling chains were avoided yet the modulus and molecular weight between cross-links could be varied either by changing the molecular weight of the PDMS macromonomer or by altering the quantity of cross-linker. Cure time was not used as a method for controlling the network properties to avoid the possibility of cure reactions continuing at room temperature to give lenses with time dependent properties.

Mechanical-property measurements were performed on the gels to demonstrate that their chemistry and properties were well behaved. The modulus of each lens was determined using the JKR method by contacting the lenses to silicon substrates that were coated with a tethered PS layer. A typical loading and unloading curve for a PDMS lens on a tethered PS substrate, shown in Figure 2, illustrates that the lenses were free from hysteresis and that the behavior corresponded

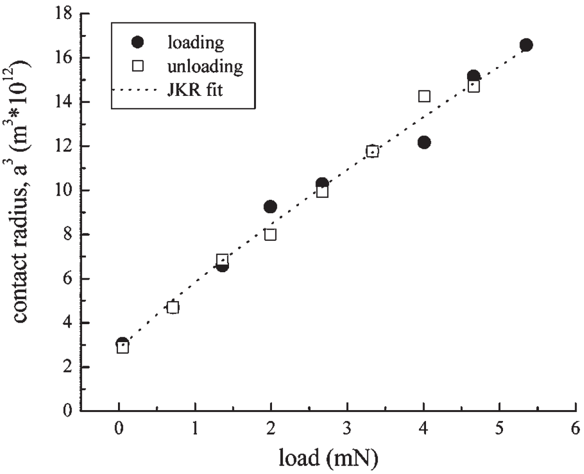


FIGURE 2 JKR loading and unloading curves for a 28KR13 PDMS lens in contact with an end-tethered polystyrene substrate. The fit to Equation (2), used to obtain K and M_c values, is shown as the dotted line.

TABLE 4 Characteristics of PDMS Lenses Used in Adhesion Studies [P(MHS-co-DMS) Crosslinker]

Lens	K (MPa)	M_c (g/mol)	Sol (wt.%)
PDMS6KR13SiH	2.73 ± 0.09	4,700	2.7
PDMS28KR13SiH	1.22 ± 0.04	10,500	0.46

TABLE 5 Characteristics of PDMS Lenses Used in Adhesion Studies [P(VMS-co-DMS) Crosslinker]

Lens	K (MPa)	M_c (g/mol)	Sol (wt.%)
PDMS6KR13vinyl	1.97 ± 0.16	6,500	0.12
PDMS28KR13vinyl	0.91 ± 0.03	14,100	0.54

well with the predictions of the JKR theory. Analysis of these JKR experiments provided estimates of the lens properties summarized in Tables 4 and 5. The uncertainties in K and W for individual lenses were taken as twice the standard error of the fitted parameters (95% confidence intervals). Where several measurements on one type of lens were taken, the reported values for K and W are the weighted averages. The errors involved in the two-parameter fit were determined by a sensitivity analysis of the JKR equation as described in detail in reference 31.

A theoretical value for W between a PDMS lens and a tethered PS substrate can be calculated from the definition of the work of adhesion,

$$W = \gamma_{\mathrm{PS}} + \gamma_{\mathrm{PDMS}} - \gamma_{\mathrm{PS-PDMS}} \tag{4}$$

where the surface tensions, γ_{i}, for PS and PDMS are 40.7 [36] and 21.7 mJ/m^2 [34, 37], respectively. In previous work [33], a value of 5 mJ/m^2 was found for the interfacial tension, $\gamma_{\mathrm{PS\text{-}PDMS}}$, between PS and PDMS. These values yield a predicted value of 57.4 mJ/m^2 for the work of adhesion between PS and PDMS. A weighted average of the data obtained for all 6KR13SiH lenses yields a value for W of 57 (+/−6) mJ/m^2.

The molecular weight between cross-links, M_c, was calculated from the modulus using the relationship obtained from the statistical theory of rubber elasticity [38, 39],

$$G = \frac{\rho RT}{M_c} \tag{5}$$

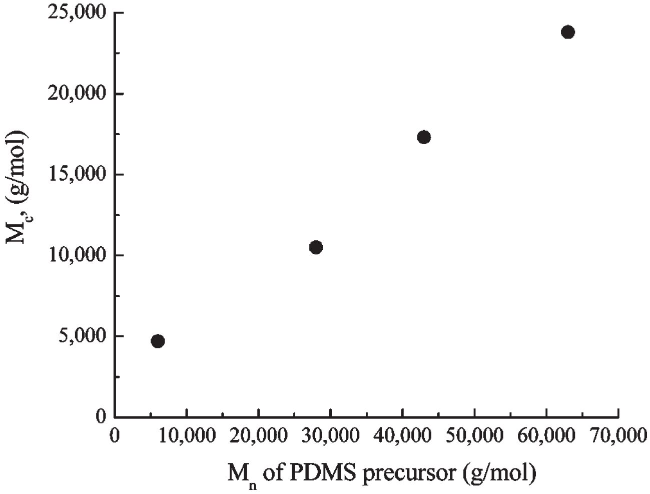


FIGURE 3 Effect of vinyl-terminated PDMS macromonomer molecular weight on M_c for cured PDMS lenses with $R = 1.3$.

where ρ is the density of the elastomer, T is the absolute temperature, and R is the gas constant. Figure 3 shows the variation in M_c with the molecular weight of the divinyl-terminated PDMS macromonomer cured with P(VMS-co-DMS) at constant molar ratio of vinyl to silane. The linear relationship confirms that the curing chemistry for this system of gels has proceeded as anticipated and that the gels exhibit the expected properties. The dependence of M_c on the ratio of cross-linker to precursor is shown in Figure 4. Again, the behavior is as expected except for the loosest networks with highest M_c. These latter gels did not exhibit good mechanical integrity and were, therefore, not employed in the adhesion testing. The amount of solvent used to dilute the PDMS mixtures during curing also effects the resultant M_c. This effect is shown in Figure 5 for two molecular-weight PDMS precursors at a constant ratio of cross-linker. It can be seen that as more solvent is added, the M_c tends to increase. This can be explained by the fact that networks created by cross-linking in a swollen state will collapse after curing to form networks with fewer trapped physical entanglements than the equivalent network formed in the dry state [40].

The mechanical-property characterizations of the PDMS gels demonstrate that the chemistry employed in their fabrication is well behaved and that their properties correspond well with theoretical expectations. The moduli of these lenses are, thus, reliable and well

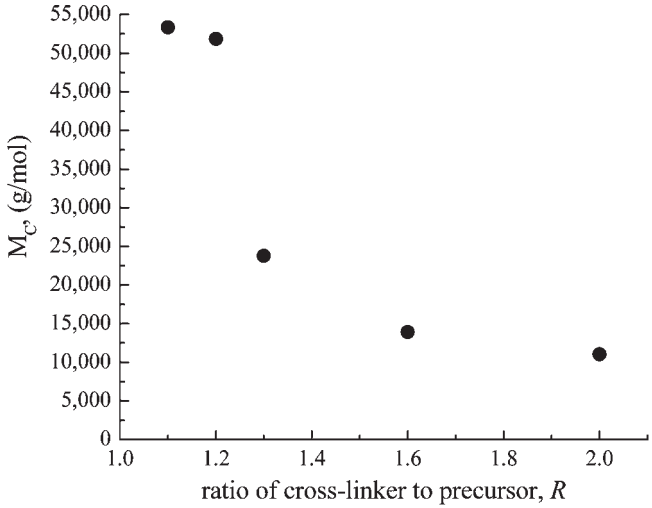


FIGURE 4 Effect of cross-linker ratio on M_c for lenses made from vinyl-terminated PDMS macromonomers (DMS-V41).

understood, an important requirement for subsequent application of these lenses to examine adhesion toward functional substrates.

The presence of residual functionality in the lenses after curing was examined with ATR-FTIR and Raman microscopy (spectra are not shown for sake of brevity and can be found in reference 31). SiH bands at 910 cm^{-1} and 2160 cm^{-1} were clearly seen for PDMS6KR13SiH but were not resolvable for the PDMS28KR13SiH gel even though silane was in excess. The R13 vinyl gels produced with P(VMS-co-DMS) in excess do show C–H stretch bands at 3053 cm^{-1} characteristic of the presence of residual vinyl groups. Unfortunately, the weak signals obtained did not allow for quantitative analysis of the concentration of residual functional groups or measurements of interfacial reaction rates.

Adhesion Measurements with Reactive Substrates

Figure 6 shows the fracture toughness for nonpoisoned PDMS28-KR13SiH lenses in contact with PSPB91P films of various thicknesses. For this combination of lens and substrate significant chain interpenetration is not probable because the substrate and lens are chemically dissimilar, but there is the possibility of a chemical reaction between residual silane groups in the lens and vinyl groups on

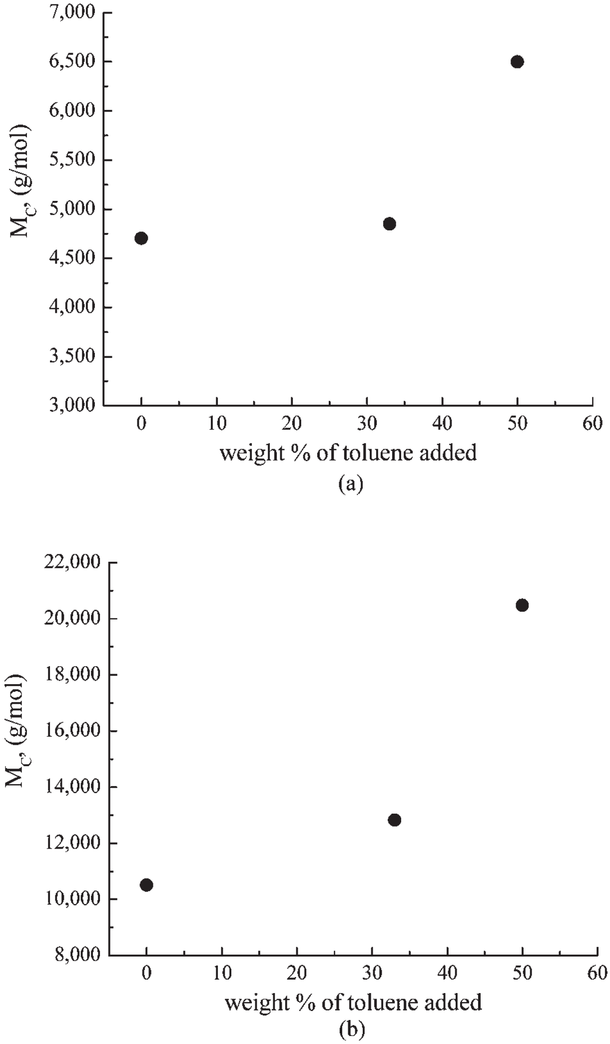
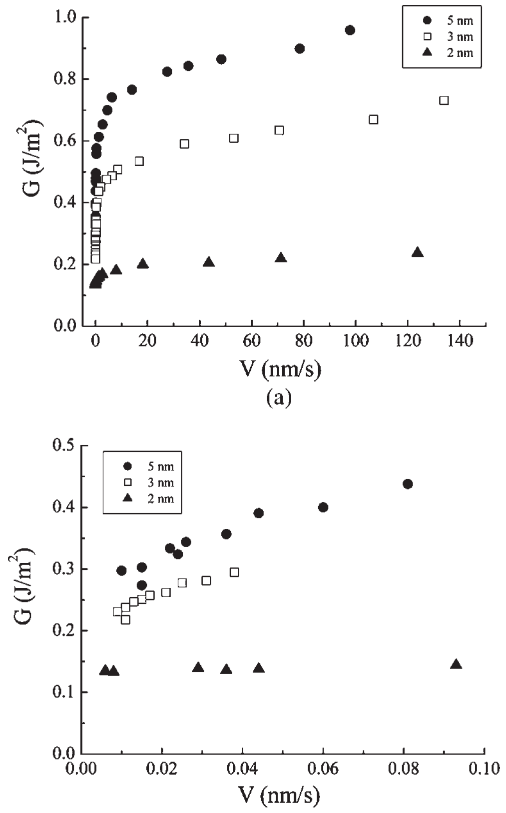


FIGURE 5 Effects of solvent present during curing on M_c for lenses prepared from vinyl-terminated precursors at a cross-linker ratio of $R = 1.3$: a) DMS-V21, b) DMS-V31.

the block copolymer modified substrate. The adhesion is clearly augmented by the presence of the block copolymer film, consistent with the expected occurrence of hydrosilylation reactions between residual silane groups in the PDMS lens and vinyl groups in the P(S-b-B) copolymers.



(a)

(b)

FIGURE 6 Fracture toughness as a function of crack velocity for nonpoisoned 28KR13SiH lenses in contact with PSPB91P films: a) high-velocity regime, b) low-velocity regime.

To confirm that hydrosilylation reactions are the origin of the observed adhesion enhancement, JKR testing was performed using two types of lenses: PDMS28KR13SiH lenses that can react with the substrate and poisoned PDMS28KR13 vinyl lenses. The latter lenses should not be able to react with the vinyl functional substrate *via* hydrosilylation because they do not contain significant silane functionality and because the platinum catalyst for hydrosilylation has been poisoned with a thiol. Figure 7 compares *G versus V* curves for two types of lenses in contact with PSPB91P. It is clear that the adhesion enhancement for the poisoned PDMS28KR13 vinyl lenses is much lower than for the nonpoisoned PDMS28KR13SiH lenses, consistent

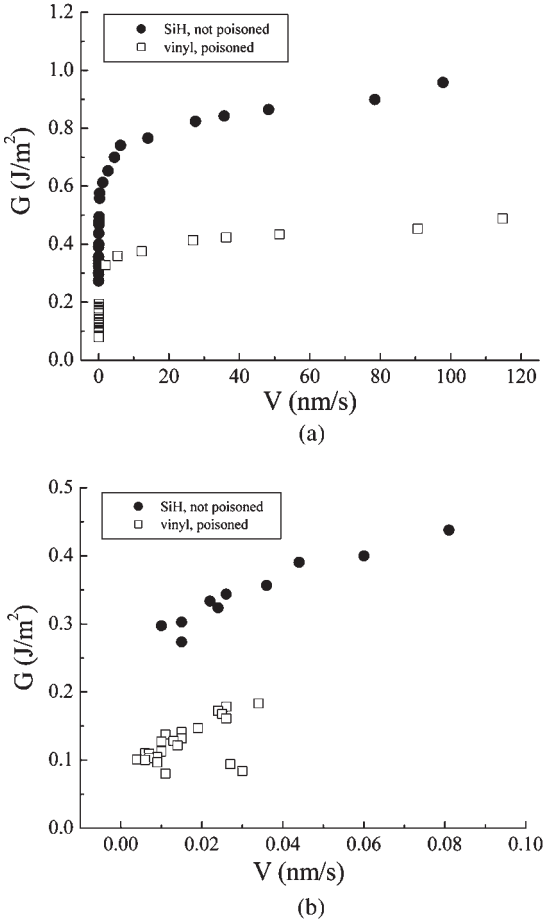


FIGURE 7 Fracture toughness as a function of crack velocity for nonpoisoned 28KR13SiH and poisoned 28KR13 vinyl lenses in contact with a 5-nm-thick PSPB91P film: a) high-velocity regime, b) low-velocity regime.

with the expectation that hydrosilylation reactions across the interface are primarily responsible for adhesion enhancement.

The extrapolated G_0 values are shown in Figure 8. The threshold toughness is roughly linear in areal density and extrapolates to approximately $40\,\mathrm{mJ/m^2}$ at zero areal density for all types of lenses. In the absence of interfacial reactions, the threshold toughness should be equal to the work of adhesion, which is $57.1\,\mathrm{mJ/m^2}$ for a PS interface with PDMS and about $40\text{–}45\,\mathrm{mJ/m^2}$ for an interface between PB and PDMS. The extrapolated values apparent in Figure 8 are, thus,

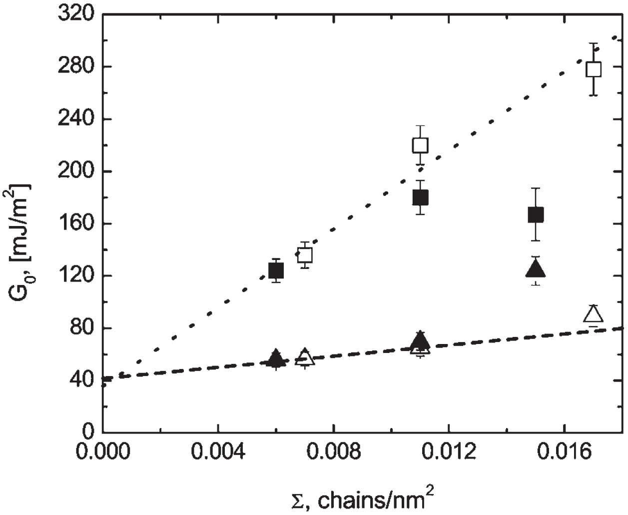


FIGURE 8 Threshold toughness as a function of block copolymer thickness for 28KR13 lenses in contact with PSPB93M and PSPB91P coated substrates. 28KR13SiH nonpoisoned lenses on PSPB93M (filled squares); 28KR13SiH nonpoisoned lenses on PSPB91 (open squares); 28KR13 vinyl poisoned lenses on PSPB93M (filled triangles); 28KR13 vinyl poisoned lenses on PSPB91P (open triangles).

similar to the work of adhesion between PB and PDMS. The slight increase in adhesion observed for the PDMS28KR13 vinyl lenses with increasing film thickness is not expected. Interfacial hydrosilylation is not possible because both sides of the interface should have only vinyl functionality. It is possible, however, that there is a small (*i.e.*, undetectable) amount of residual SiH functionality in the PDMS gels that could cause this effect or, alternatively, vinyl–vinyl reactions across the interface may also occur as have been postulated in previous studies of diene-based elastomers [6–9]. In cases where interfacial hydrosilylation reactions can occur, the adhesion is found to increase almost linearly with copolymer film thickness and is slightly higher for the polydisperse block copolymer substrates than for the monodisperse block copolymer substrates.

The effects of the dwell time on the adhesion enhancement provided by interfacial chemical reactions are reported in Figure 9 for nonpoisoned PDMS6KR13SiH and PDMS28KR13SiH lenses in contact with vinyldimethylchlorosilane self-assembled monolayers. Significant adhesion enhancement is observed for both lenses with a gradual buildup in adhesion continuing even after two weeks. Here again,

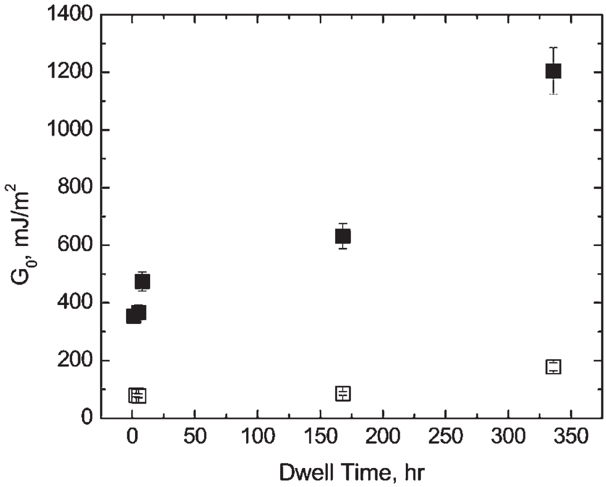


FIGURE 9 Threshold toughness as a function of dwell time for nonpoisoned PDMS lenses in contact with a vinyl functionalized surface: 6KR13SiH (open squares), 28KR13SiH (filled squares).

the enhancement is afforded by the possibility of hydrosilylation reactions between residual silane groups in the gels and surface vinyl groups on the SAM-coated substrate. Similar long-time behavior was associated with chain interpenetration in earlier studies, but the fact that interpenetration is not possible across the SAM interface suggests that the present time effect is associated with the kinetics of the interfacial reactions. The results also indicate that the interfacial fracture energy is much higher for the more loosely cross-linked elastomer gel than for the more densely cross-linked gel.

Explanations for the effects of the copolymer-film thickness and cross-link density of the elastomer gels (*i.e.*, molecular weight between cross-links) on the interfacial fracture energy can be obtained by considering the predictions of the Lake–Thomas model for elastomer failure [41]. When applied to adhesion, the model predicts that the threshold toughness should scale according to

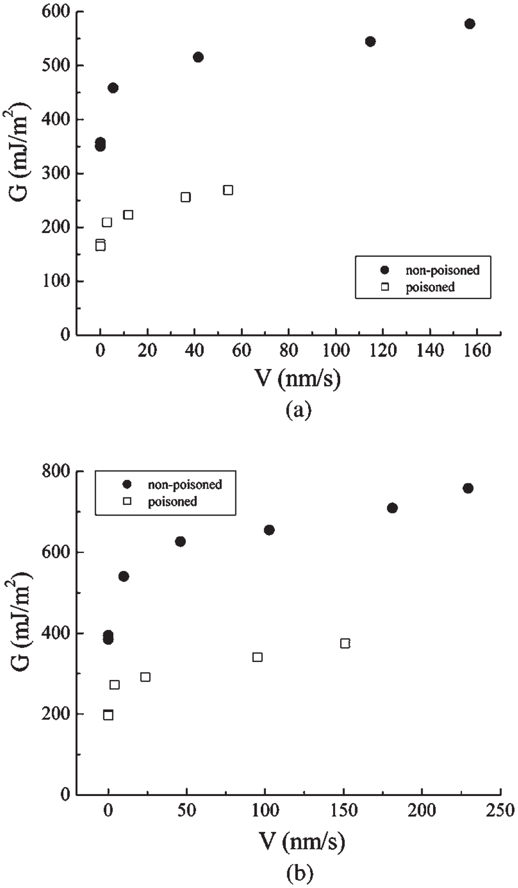
$$G_0 = \Sigma M \varepsilon \tag{6}$$

where Σ is the areal density of linker chains across the interface, M is their molecular weight, and ε is the energy required to break a bond in the linker chain. In the case of the data in Figure 9, the appropriate molecular weight for the linker will be proportional to the molecular weight between cross-links in the PDMS gel. According to Equation (6), if the areal density is constant, a looser network with higher molecular weight between cross-links should yield higher interfacial fracture energy, as is observed experimentally.

The Lake–Thomas model might also account for the observed increase in interfacial fracture energy found with increase in the P(S-b-B) block copolymer thickness. As the copolymer thickness increases, the areal density must also increase in linear fashion according to Equation (1), leading to a predicted linear increase of G_0 with copolymer thickness according to Equation (6). In addition, PB chains at the surface must orient somewhat in plane when their thickness is less than the radii of gyration and more normal to the surface for thicknesses larger than the radii of gyration. For low thicknesses, therefore, the silane group in the silicone gel can react with vinyl groups located almost anywhere along the PB copolymer sequence. For higher thicknesses, however, the PB sequences adopt more upright configurations so that vinyl groups closer to the substrate will be sterically screened from reaction and the reaction site must be located nearer to the chain end. The length of the PB linker chain might, therefore, be expected to increase with thickness of the copolymer surface layer. Two factors can, therefore, cause an increase in adhesion with copolymer thickness: the associated increase in areal density and an accompanying probable increase in the length of the PB linker chains. These two effects in concert can produce a stronger than linear dependence of fracture energy with molecular weight of the block copolymer.

The Lake–Thomas model also provides a possible explanation for the observation that polydisperse block copolymers provide a slightly higher adhesion enhancement than monodisperse copolymers of the same average molecular weight. The ends of the longer brushes are forced away from the substrate by the shorter chains and, therefore, have a higher relative concentration near the surface and higher probability of reaction. The linker chains for the more polydisperse block copolymer should, therefore, be longer on average, leading to enhanced adhesion according to Equation (6).

The adhesion behavior for PDMS gels in contact with a substrate prepared by coating α,ω-monomethoxy PDMS onto a silicon wafer is shown in Figure 10. A high level of adhesion is obtained for both the 28KR13SiH and the 43KR13SiH nonpoisoned lenses. The molecular weight of the PDMS used is only 1000 g/mol, well below the entanglement molecular weight of 8,100 g/mol [42] so chain interpenetration cannot be the cause of the adhesion. The PDMS is monomethoxy terminated at both ends so the PDMS brushes formed will have both loop and tail configurations when tethered to the surface. The



(a)

(b)

FIGURE 10 Fracture toughness as a function of crack velocity for PDMS lenses in contact with monomethoxy-terminated tethered PDMS brushes (1000 g/mol): a) 28KR13SiH, b) 43KR13SiH.

end-functional tails have the potential to react with the PDMS gels through their methoxy end groups *via* a condensation reaction with residual SiH groups in the PDMS gels. This reaction proceeds with the elimination of methanol. Poisoning the platinum catalyst that promotes hydrosilylation reactions does reduce the amount of adhesion, as shown in Figure 10; however, significant adhesion remains as shown by the G_0 values in Table 6.

Figure 11 shows the *G versus V* curve for nonpoisoned PDMS63KR13SiH lenses against a series of α,ω-hydroxy-terminated PDMS brushes tethered on silicon wafers. These surfaces are similar

TABLE 6 Threshold Toughness for PDMS Lenses in Contact with End-Tethered PDMS (α,ω-Monomethoxy Terminated, 1000 g/mol) on a Silicon Wafer

Lens	M_c (g/mol)	G_0 (mJ/m^2), not poisoned	G_0 (mJ/m^2), poisoned
PDMS6KR13SiH	10,500	361 ± 25	170 ± 12
PDMS28KR13SiH	17,300	386 ± 25	198 ± 13

to those used by Leger *et al.* [11, 12, 43]. Significant adhesion enhancement was observed for the α,ω-hydroxy-terminated PDMS brushes as can be seen by the resultant G_0 values displayed in Table 7. The result for the 4200 g/mol brush, with a molecular weight that is clearly below the molecular weight for entanglements, is particularly interesting. For this material the enhancement cannot be the result of chain interpenetration and must be associated with interfacial chemical reactions. Poisoning the residual platinum catalyst in the lenses does not reduce the adhesion enhancement because hydroxyl groups do not participate in platinum-catalyzed hydrosilylation reactions. Other

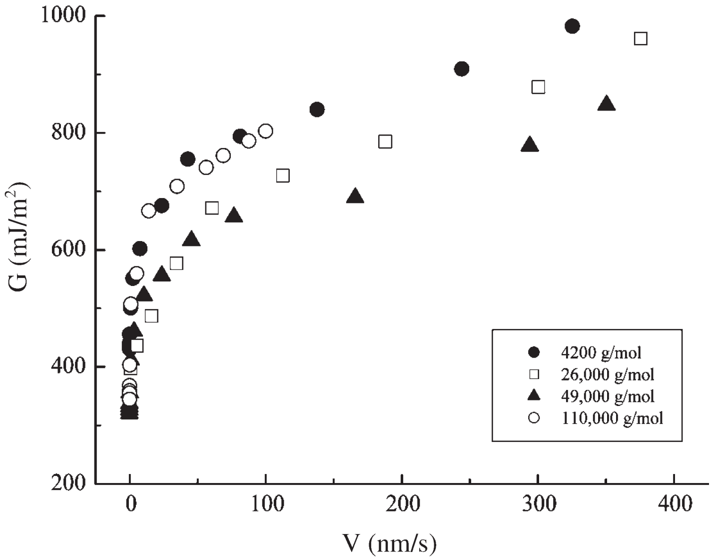


FIGURE 11 Fracture toughness as a function of crack velocity for nonpoisoned 63KR13SiH lenses in contact with hydroxyl-terminated PDMS brushes tethered to silicon wafers. The insert indicates the molecular weight of the PDMS brushes.

TABLE 7 Threshold Toughness for PDMS63KR13SiH Lenses in Contact with End-Tethered PDMS Brushes (α, ω-hydroxy Terminated) on a Silicon Wafer

M_n (g/mol)	Film thickness (nm)	Σ (chains/nm^2)	G_0, (mJ/m^2), not poisoned	ε Apparent J/bond × 10^{20}
4200	3.0	0.07	431 ± 20	5.4
26,000	5.1	0.019	328 ± 15	2.5
49,000	8.0	0.016	320 ± 15	1.5
110,000	12.3	0.011	345 ± 17	1.1

mechanisms, such as condensation reactions, are possible, however, between the PDMS lenses and surface-bound hydroxyl groups. When polybutadiene lenses were tested against these same brushes (data not presented herein, see reference 31) no adhesion was observed, demonstrating that vinyl groups play no role in these reactions.

The adhesion data for the hydroxyl-terminated PDMS brushes provide some insight into the number of linker chains that might form across the interface. The dissociation energy for the Si–O bonds within PDMS is 8.9×10^{-19} J whereas that of C–C or Si–C bonds that may reside within the linker molecule is 6.1×10^{-19} J. The estimated chain scission energies (Table 7) are about one order of magnitude lower than these bond energies. Considering that about one half of the chains will adopt loop configurations with both ends tethered to the substrate, this comparison would suggest that about one in 5 to 10 PDMS brush chains are covalently bound to the PDMS gel.

Nonpoisoned and poisoned PDMS63KR13SiH lenses were also tested using clean silicon wafers as substrates. In this case, reactions are possible with surface silanol groups on the substrate. Poisoning the lenses reduced the adhesion from $1020 \pm 50\,\mathrm{mJ/m^2}$ to $490 \pm 20\,\mathrm{mJ/m^2}$, a rather surprising result. It may be that platinum plays some role in catalyzing silane–silanol reactions, or perhaps that excess thiol from the catalyst-poisoning reaction interacts with the bare silicon wafer in a way that passivates surface silanol groups. In any case, significant adhesion enhancement is observed even after catalyst poisoning.

The results of JKR testing on the adhesion between PDMS elastomers and a variety of functional substrates clearly demonstrate that PDMS gels are capable of a variety of interfacial reactions at room temperature and that poisoning the platinum catalyst does not prevent all chemical reactions. Some of the possible reactions that can occur are shown in Figure 12. Interfacial hydrosilylation is clearly responsible for the adhesion between PDMS lenses and P(S-b-B)

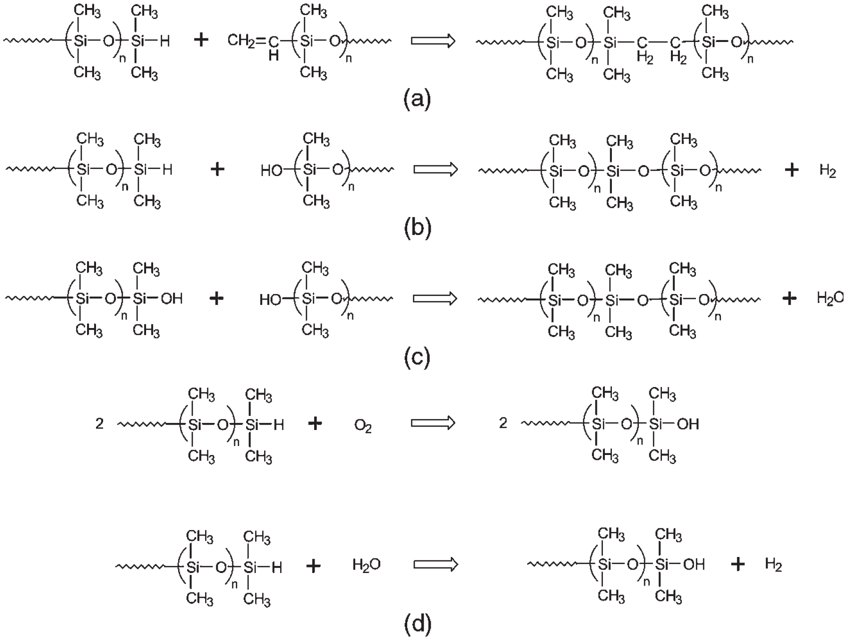


FIGURE 12 Possible chemical reactions involving PDMS lenses and functional substrates: a) hydrosilylation, b) dehydrogenative coupling, c) condensation, d) hydrolysis.

copolymers and also plays a significant role in the hysteresis observed in self-adhesion experiments between PDMS gels [23–30].

The adhesion enhancement observed between PDMS gels and α,ω-hydroxy-terminated PDMS or α,ω-monomethoxy-terminated PDMS brushes, however, cannot be explained by the occurrence of hydrosilylation reactions. In this case, adhesion enhancement requires first the formation of a PDMS brush tethered at one end to the surface by a reaction between terminal hydroxyl or methoxy groups on the α,ω-functional PDMS and silanol groups on the silicon-wafer surface. Hydroxyl and methoxy groups can tether the first end of the brush to the substrate by a condensation reaction (*e.g.*, Figure 12c) liberating water or methanol, respectively. To form a linker chain, the second, untethered brush end (*i.e.*, not reacted to the substrate) must then react with residual SiH groups in the PDMS gel. This can occur by a dehydrogenative coupling reaction as shown in Figure 12b for the hydroxyl-terminated brush. This reaction normally requires the presence of a metal salt such as bis(2-ethyl-hexanoate) tin or zinc octanoate as catalyst [44], but is also known to be catalyzed at room temperature by chloroplatinic acid. It is possible, therefore, that the platinum catalyst used in the synthesis of the PDMS gels could catalyze this reaction. Alternatively, if residual SiH groups in the PDMS gel hydrolyze (Figure 12d) to form silanol groups, the gel can form linker chains by reaction with either hydroxyl or methoxy groups on the brushes by a condensation reaction. It is debatable, however, whether the hydrolysis of SiH groups can occur at room temperature and ambient pressure, and there is no evidence for the formation of silanol groups in the FTIR-ATR spectra of the extracted PDMS gels. One final possibility is that hydrogen-bonding interactions between the substrate and gel might also lead to an enhancement in the fracture toughness.

CONCLUSIONS

The influence of interfacial reactions on the adhesion behavior between functional PDMS elastomers and functional substrates has been investigated using the JKR technique. To emphasize interfacial chemistry effects, the interfaces studied have been designed to minimize the possibility of significant chain-interpenetration effects. We find that a variety of silicone reactions can occur at the interface and that they provide significant adhesion enhancement. Hydrosilylation reactions between residual vinyl or hydride functionality in the PDMS elastomer gels and complementary functionality on the substrate are particularly effective in forming linker chains that span the interface. The fact that adhesion enhancement is almost absent when the platinum catalyst is poisoned provides supporting evidence that hydrosilylation reactions lead to adhesion enhancement. In systems that incorporate hydroxyl, methoxy, and silanol functionality on the substrate surface, significant adhesion enhancement is observed even when the platinum catalyst is poisoned, evidence for the formation of interfacial bonds by condensation, hydrolysis, and dehydrogenative coupling reactions. In most cases studied, the level of adhesion enhancement produced by interfacial reactions is consistent with the general predictions of the Lake–Thomas model for elastomer failure. That is, the threshold toughness generally scales with the length and areal density of linker chains that form across the interface.

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