Improved Adhesion of Silicone Rubber to Polyurethane by Induced Surface Reconstruction

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ABSTRACT: Induced surface reconstruction of silicone rubber by blending polydimethylsiloxane (PDMS) reactants with bifunctional PDMS-hydroxyl terminated polybutadiene (PDMS-*b*-HTPB) copolymers and curing with appropriate mold material was attempted to improve the adhesion of chemically inert silicone rubber to polyurethane (PU). Surface characterization using Fourier transform infrared-attenuated total reflectance indicated that the surface of the silicone rubber possessed a controlled amount of HTPB. The surface was enriched with HTPB by using mold materials having high critical surface tension, such as aluminum. A dynamic surface rearrangement occurred during a 1-h heating cycle at 70°C, changing from an HTPB-enriched surface to a PDMS-enriched surface. The peel strength between the silicone rubber and PU was found to increase with decreased propanol residue and with an increase in critical surface tension of the molding materials. The increased content of surface HTPB was suggested to account for the improved adhesion of silicone rubber to PU. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1669–1675, 1998

Key words: surface reconstruction; adhesion; silicone; polyurethane; FTIR-ATR

INTRODUCTION

The unusual heat, electrical, weather, and low-temperature resistance properties of silicones, i.e., room temperature–vulcanizable (RTV) silicone rubber, have manifested themselves in a wide variety of applications.[1–3] They are used as engineering materials for manufacturing electrical apparatus and machines. Strong adhesion of silicones to the target matrix is a requirement for long product life. The inherently hydrophobic nature of silicones, coupled with their ability to segregate to the surface, facilitates their use as a surface modifier for other materials. This prop-erty has been exploited in the preparation of silicone-modified polyesters[4]; the synthesis of polydimethylsiloxane (PDMS) and polystyrene copolymers[5]; polyimidesiloxane segmented copolymers[6]; triblock siloxane copolymers used as surface modifying additives[7]; blood-compatible polyurethane (PU)-polysiloxane graft copolymers[8]; and the surface treatment of fumed silica for use as antifoaming compounds.[9] Small amounts of the copolymers (ca. 1% by weight) could be added to different polymers to alter their surface properties. The air–polymer surface of the resulting polymer system is usually dominated by the low surface-energy siloxane,[7,10] preventing adhesion to polar materials. This phenomenon of surface segregation of a component with a low surface energy in multicomponent polymeric materials attracts attention to the analysis of polymer surfaces and the modifications of their properties.[11–15]

Surface modification of polymers by chemical, photochemical, corona, plasma, and high-energy radiation treatments are currently used to increase the polarity of polymer surfaces, thus enhancing their adhesion to immiscible polymers.[16,17] An alternative means of modifying polymer surface is by blending with diblock copolymers, where one block interacts favorably with the base matrix and the other block with the target matrix.[18] The polymeric surface can form ordered, oriented layers at the surface during subsequent curing.[19] The part of such copolymers with a low critical surface tension is readily miscible with the silicone base matrix, whereas the other part interacts favorably with the more polar matrix. Both blocks can anchor the copolymer into the respective substrate, which ensures permanency of the surface modification and increases adhesion between two immiscible polymers.

In this article we describe a specific bond between silicone rubber and PU using an induced surface reconstruction approach. This was realized by blending small amounts of bifunctional PDMS-hydroxyl terminated polybutadiene (HTPB) copolymers with PDMS, then casting them on appropriate molding plates during curing to induce the formation of desired surface property. The PDMS-b-HTPB copolymers at the surface of the silicone rubber can serve as a bridge between the silicone rubber and PU. The PDMS at one end mixes well with the PDMS base matrix, whereas the HTPB segregating to the surface participates in the crosslinking reaction of the PU target matrix. The surface composition of the induced silicone rubber was investigated using Fourier transfer infrared-attenuated total reflectance (FTIR-ATR).[20,21] Peel strength[22] was used to measure adhesion of silicone rubber to PU. The correlation between surface composition and peel strength suggests a cause for improved adhesion of silicone rubber to PU.

EXPERIMENTAL

Materials

Dichlorodimethylsilane (DCDMS) and HTPB were obtained from Petrach System (Bristol, PA). Hydroxyl-terminated PDMS was obtained from Dow Corning (Midland, MI). HTPB and PDMS were dried in a rotary flask under vacuum at 70°C for 4 h before use. The number-average molar mass ($\overline{M}_n$) and OH values are 2,800 and 0.82 for HTPB, 3,400 and 1.0 for PDMS, respectively. Toluene was dried over sodium at 80°C overnight, followed by distillation using benzophenone as an indicator. Other reagents were purified by the usual methods. The silicones used were commercially available RTV silicones, RTV-700, from General Electric (Waterford, NY).

The molds used were Al, Fe, low-density polyethylene (PE, density = 0.95 g/cm³), and Teflon (Du Pont TFE-Teflon, Wellington, DE). The surfaces of the Al and Fe were sanded and degreased with chloroform prior to use. All other molds were used as received.

Synthesis of PDMS-b-HTPB Copolymers

A total of 25.2 g of PDMS and an excess amount of DCDMS (3.2 g; molar ratio PDMS : DCDMS = 1 : 3.4) were dissolved in 76 g of toluene. Several drops of pyridine were added. The reaction was continued with stirring for 4 h at 80°C. A viscous fluid of chlorine terminated PDMS (CTPDMS) was obtained after the residual solvent and DCDMS were removed from the reaction flask by distillation. A total of 80 g of toluene and 17.6 g of HTPB (molar ratio CTPDMS : HTPB = 1 : 1) were carefully added into the reaction flask, followed by the addition of several drops of pyridine. The reaction mixture was stirred in a thermostatted bath at 100°C for 4 h and terminated by the addition of water. The product (PDMS-b-HTPB copolymers) was isolated and purified by repeatedly washing with deionized distilled water.

Induced Surface Reconstruction of Silicone Rubber

The RTV-700 was homogeneously mixed with $Si(OC_3H_7)_4$ curing agents (molar ratio RTV-700 : $Si(OC_3H_7)_4$ = 10 : 1), about 1% (wt %) PDMS-b-HTPB copolymers, and dibutyl–tin dilaurate catalyst in a beaker by stirring at ambient conditions. The samples were cured at room temperature for 24 h between smooth-surface molds in a hydraulically operated press at atmospheric pressure to induce surface reconstruction of the silicone rubber. The rubber was removed from the mold and placed under vacuum for 24 h to remove the propanol by-products.

Adhesion of Native and Surface Reconstructed Silicone Rubbers to PU

The PU target matrix was prepared by mixing HTPB, toluylene-2,4-diisocyanate (TDI), and an-

Scheme 1

reactions (1)–(6):

(1) $OH(Si-O)_n H$ with CH_3 side groups $+ 2Cl-Si-Cl$ (2) $\xrightarrow[\text{Toluene}]{\text{Pyridine}}$ $Cl(Si-O)_{n+1}Si-Cl + 2HCl$ (3)

(3) $Cl(Si-O)_{n+1}Si-Cl + HO(CH_2CH=CHCH_2)_l(CH-CH_2)_m OH$ (4) $\xrightarrow[\text{Toluene}]{\text{Pyridine}}$

cis- & trans-

(5) $Cl(Si-O)_{n+2}(CH_2CH=CHCH_2)_l(CH-CH_2)_m OH + HCl \xrightarrow{+H_2O}$

(6) $HO(Si-O)_{n+2}(CH_2CH=CHCH_2)_l(CH-CH_2)_m OH + HCl$

timony (III) oxide (Sb_2O_3) in the weight ratio of 100 : 7.08 : 180. The mixtures were poured on top of the silicone rubbers (native and surface-reconstructed). The curing reaction of PU was continued for 5 days at 70°C under a hydraulically operated press at atmospheric pressure, unless otherwise specified.

Measurements and Instruments

The size (expressed as radius of gyration which is the root mean square distance of the elements of the polymer chain from its center of gravity), $\overline{M_n}$, silanol content, and alcohol contents of the PDMS-*b*-HTPB copolymers and the corresponding reactants (CTPDMS and HTPB) were characterized using gel permeation chromatography (GPC) (in toluene versus polystyrene standards), vapor pressure osmometry (VPO), and Karl Fischer titration.[23] The GPC was measured using a Waters ALC/GPC-150C equipped with a column equally packed with 10^5, 10^4, 10^3, and 500 Å μ-Styragel operated at 30°C and 1 mL/min flow rate. The size of the polymer was determined by comparing its retention time with that of polystyrene standards with known size. $\overline{M_n}$ by VPO was determined in toluene using a Knauer instrument and calibrated with standard PPG 2000 samples. Karl Fischer titration was carried out using a Metrohm K.F. Processor model 658. The surface composition of the silicone rubber was obtained by analyzing the FTIR-ATR spectra. The spectra

were recorded with a Nicolet 5DX FTIR and scanned between 800 and 4,000 cm^{-1} at a resolution of 4 cm^{-1}. A Ge prism with a 45-degree face cut was used as the internal reflectance element. A total of 200 scans were obtained to yield the average spectrum. The bonding strength between the silicone rubber and PU was obtained according to the ASTM-D903-49 peel test method[22] with an Instron. Static contact angles of water droplet were measured at 25°C at by an NRL-Moel-A-100 contact angle geniometer.

RESULTS AND DISCUSSION

Synthesis and Characterization of PDMS-*b*-HTPB Copolymers

The PDMS-*b*-HTPB copolymers were synthesized according to the method presented in Scheme 1. The backbone component of CTPDMS (**3**) was prepared by reaction of PDMS, having a silanol end group (**1**) with DCDMS (**2**), followed by chain extension with HTPB (**4**) to form the PDMS-*b*-HTPB copolymer (**6**). The $\overline{M_n}$ of the PDMS-*b*-HTPB copolymers was controlled by terminating the chain extension of intermediate products (**5**) via hydrolysis.

The size and $\overline{M_n}$ of the PDMS-*b*-HTPB copolymers product, and the DCPDMS and HTPB reactants obtained by GPC and VPO, respectively, are shown in Table I along with the Si-OH and R-OH content (wt %). The molar mass and size, as well as the reduction in R-OH content, indicate that the PDMS-*b*-HTPB copolymer is predominantly a diblock copolymer.

Adhesion of Native and Surface Reconstructed Silicone Rubbers to PU

Trace amounts of PDMS-*b*-HTPB copolymers and $Si(OC_3H_7)_4$ curing agents were mixed with RTV-700, followed by condensation curing using dibu-

Table I   Properties of PDMS-*b*-HTPB Copolymers, DCPDMS, and HTPB

Polymer	Size (Å)	$\overline{M_n}$ (g mol^{-1})	Si-OH (wt %)	R-OH (wt %)
CTPDMS	263	3,400	—	—
HTPB	157	2,800	—	0.82
PDMS-*b*-HTPB copolymers	410	6,800	0.28	0.22

Scheme 2

tyl–tin dilaurate catalyst (Scheme 2) under appropriate conditions to prepare native and surface-reconstructed silicone rubbers. The propanol by-product was expected to react more rapidly with the TDI than the HTPB due to the mobility of propanol. The silicone rubbers were therefore stored under various conditions before subsequent PU curing reactions to investigate the effect of propanol on the peel strength between silicone rubber and PU.

Figure 1 shows the peel strength between silicone rubber and PU as a function of the storage time of the surface-reconstructed silicone rubber at 25°C in ambient, dried box, and vacuum (about 10 torr) conditions. The mold used was Al. The PU adhered to the silicone rubber after the specified storage time. The peel test was performed after the PU was cured for 5 days at 70°C. Vacuum storage conditions always yielded a higher peel strength for the silicone rubber/PU layers. The peel strength was observed to increase with increasing storage time, regardless of the storage condition, with the maximum value obtained after 24 h of storage time. The dependence of peel strength on storage time and condition could, presumably, be attributed to the propanol by-products from the condensation-curing reaction. The amounts of propanol residues in the silicon rubber were found to decrease in the order of ambient, dried box, and vacuum storage condition and with increasing storage time. This was consistent with the expectation that the amount of volatile propanol that escaped from the silicone rubber would increase under reduced pressure and with increased exposure time. The final amount of propanol residue found in the silicone rubber was monitored at 4-h storage intervals, up to 48 h, in

vacuum. A nearly constant value of about 2% was obtained after 24 h. Therefore, it can be concluded that the peel strength between the silicone rubber and the PU was strongly dependent on the amount of propanol residue from the RTV-700 condensation-curing reaction. All silicone rubbers studied thereafter were, therefore, stored in vacuum at 25°C before subsequent processing.

The effects of mold materials on the peel strength between silicone rubber and PU as a function of storage time are shown in Figure 2. Significantly higher peel strength was observed for Al-treated silicone rubber. The peel strength continued to increase and reached a maximum value of 1.2 kg/cm after 2 days. With longer storage time it decreased to a nearly constant value of 0.6 kg/cm. A similar trend was observed for Teflon-treated silicone rubber but with significantly lower peel strength. For example, the peel strength reached a maximum value of 0.2 kg/cm after 2 days, decreased to 0.1 kg/cm after 10 days, and was constant thereafter. The peel-strength curve was quite different for the native silicon rubber, i.e., without any molding material. The peel strength increased slowly from zero to 0.1 kg/cm after 10 days and remained constant thereafter.

The effects of mold materials on the peel strength were investigated further using other mold materials. The maximum peel strength be-

Figure 1 Storage time and condition dependence of the peel strength between Al-treated silicone rubber and PU at 25°C.

Figure 2 Effect of mold materials on the peel strength between silicone rubber and PU as a function of storage time at 25°C.

tween silicone rubber and PU and the critical surface tension (γ_c) of these mold materials are listed in Table II. The γ_c values are related to the surface composition. In principle, a small change in the polarity, or hydrophilicity, of the surface results in a clear change of its γ_c. The γ_c values[24] therefore reflect the hydrophilic nature of the mold materials. It is clear that the higher the γ_c of the mold material, the higher the peel strength between the surface-reconstructed silicone rubber and PU. This indicates that the hydrophilic nature of PE, Al, and Fe have caused a segregation of the high surface-energy HTPB blocks to the surface, as opposed to the lower surface-energy PDMS blocks. The HTPB blocks that have segregated to the surface of the silicone rubber may subsequently participate in the end-linking reaction of HTPB/TDI/Sb_2O_3 mixture to form the PU. The increased peel strength may therefore be attributed to the surface enrichment of HTPB blocks. The decrease in peel strength with increased storage time for Al-treated silicone rubber indicates that the system is in dynamic equilibrium. The PDMS blocks have a propensity to segregate to and accumulate at the silicone rubber–PU interface. This weakens the interfacial bonding. The segregation of PDMS blocks to the surface could be accelerated by heat. Thus when the Al-treated silicone rubber was heated at 70°C for 1 h followed by adhesion to PU, at room tem-

perature the peel strength become zero due to the decrease in the adhesion of silicone rubber to PU. However, the original peel strength of about 1.2 kg/cm could be recovered when the heated Al-treated silicone rubber was cooled to room temperature (with the Al mold on) prior to adhesion to PU. These observations indicate that the adhesion of silicone rubber to PU is influenced by the presence of HTPB blocks extruding out of the silicone rubber which, in turn, depends on the temperature of the system prior to adhesion to PU. The increased concentration of surface HTPB accounted for the improved adhesion of silicone rubber to PU.

Surface Characterization of Silicone Rubber by FTIR-ATR

Figure 3 shows the FTIR-ATR spectra of silicone rubber containing no PDMS-*b*-HTPB copolymers, Al-treated silicone rubber containing PDMS-*b*-HTPB copolymers, and Teflon-treated silicone rubber containing PDMS-*b*-HTPB copolymers. The depth of penetration in the region of C—H stretching at 3,000 cm^{-1} is $\sim$ 0.1 μm for the Ge element.[20] The intensity of the CH_2 symmetric stretching at 2,850 cm^{-1} was therefore used to represent the HTPB surface concentration. The ratio of HTPB at the surface in Al-treated and Teflon-treated silicone rubber was determined using the ratio of peak intensities at 2,850 cm^{-1} after subtracting the spectrum of silicone rubber containing no PDMS-*b*-HTPB copolymers. The background-corrected peak intensities (in absorbance units) at 2,850 cm^{-1} of Al-treated and Teflon-treated silicone rubber spectra were 0.043 and 0.032, respectively. A simple calculation in-

Table II   Peel Strength Between Silicone Rubber and PU for Different Mold Materials and Critical Surface Tension of the Mold Materials

Mold Materials	Critical Surface Tension at 20°C (dyn/cm)[a]	Peel Strength (kg/cm)
Air	—	0.1
Teflon	18.5	0.2
Polyethylene	31.0	1.1
Al	$\sim$ 40	1.2
Fe	$\sim$ 40	1.3

[a] The critical surface tension for PDMS is 24 dyn/cm.

Figure 3 The FTIR-ATR spectra of (a) silicone rubber containing no PDMS-*b*-HTPB copolymers, (b) Al-treated silicone rubber containing PDMS-*b*-HTPB copolymers, and (c) Teflon-treated silicone rubber containing PDMS-*b*-HTPB copolymers. The arrows mark the CH_2 symmetric stretching at 2,850 cm^{-1}.

dicates that the surface concentration of HTPB in Al-treated silicone rubber is 34% greater than that in Teflon-treated silicone rubber. This suggests that the improved adhesion of silicone rubber to PU could be attributed to an induced surface enrichment of HTPB blocks.

Improved Adhesion of Silicone Rubber to PU

The FTIR-ATR and γ_c measurements of the silicone rubber surfaces revealed very different characteristics from those expected from the bulk structure. A "island-hole" type microphase-sepa-

rated surface structure[12] for the silicone rubber containing PDMS-*b*-HTPB copolymers was envisaged. There are several competing tendencies that determine the composition in the surface region. One is the reduction of the surface energy of the contact media surface of the silicone rubber. If RTV-700 is cured in contact with air, the PDMS domains spread over the surface due to the lower surface energy of PDMS (24 dyn/cm). In contact with Al (40 dyn/cm) during curing, the surface responds to the change of contacting media by rearranging its structure. The hydrophilic blocks (i.e., HTPB) could overcome the energy barrier and segregate to the surface for a minimized overall free energy. The surface becomes HTPB-enriched. The measured static contact angles using deionized water are 114 degrees, 101 to 103 degrees, and 112 to 114 degrees for the native, Al-treated, and Teflon-treated silicone rubber containing PDMS-*b*-HTPB copolymers, respectively, which agrees with this suggestion. In addition, the crosslinking density of the base matrix (i.e., the silicone rubber which might determine the ease of segregation) as well as the extent of reaction with the target matrix (i.e., the PU which might determine the stability of anchoring) might also effect the preservation of HTPB blocks on the surface. Considering these factors, improved adhesion of silicone rubber to PU could be attributed to the enrichment of HTPB blocks on the silicone rubber surface.

CONCLUSIONS

The induced surface reconstruction of silicone rubber by blending PDMS reactants with bifunctional PDMS-*b*-HTPB copolymers and curing with molds having high γ_c was used to improve the adhesion of chemically inert silicone rubber to PU. Surface characterization using FTIR-ATR indicated that the surface of the silicone rubber possessed a controlled amount of HTPB. The surface could be enriched with HTPB by using molding materials of high γ_c, such as Al. A dynamic surface rearrangement occurred during a 1-h heating cycle at 70°C from HTPB-enriched surface to PDMS-enriched surface. The extent of adhesion of silicone rubber to PU was found to increase with reduced amounts of propanol residues and increased γ_c of the molding materials. The increased concentration of surface HTPB accounted for the improved adhesion of silicone rubber to PU. The success in adhering two immiscible polymers, such as silicone rubber and PU in

this study, demonstrates the feasibility of the induced surface reconstruction method for modifying polymeric surfaces. The applicability of this method to addition-curing silicone rubbers is the subject of further study.

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