Thermal Gradient Enabled XPS Analysis of PDMS Elastomer Adhesion to Polycarbonate

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Adhesion of silicone elastomers to a variety of substrates is of significant importance because of the unique properties of polydimethylsiloxane (PDMS) that make it well suited for industrial products such as sealants, adhesives, and coatings. Further, adhesion control is of growing importance in the development of various emerging microassembly techniques such as imprint lithography or microfluidics where a Pt-cross-linked (cured) PDMS elastomer such as Dow Corning Sylgard 184 is often used. There is a significant volume of literature devoted to studies of coupling agents at interfaces.[1−15] However, there are relatively few fundamental studies of the use of reactive coupling agents as adhesion promoting additives in Pt-cured PDMS elastomers for bonding to non-silicone substrates.[16,17] Understanding the precise mechanisms acting in strongly bonded elastomers is hindered by the fact that a well-adhered interface, by definition, cannot be readily separated and exposed for analysis. In a prior study, significant adhesion promoter segregation was observed in Pt-cured PDMS at a polycarbonate (PC) substrate interface.[18] The segregation was markedly enhanced with the use of a partially miscible, cross-linkable interfacial enrichment additive. There, a relatively weak acrylic adhesion promoter was used to facilitate interface separation for surface analysis. To extend to strongly bonded elastomer/plastic interfaces, we now couple a high throughput thermal gradient peel test method with X-ray photoelectron spectroscopy (XPS) to study the development of adhesion with cure temperature in silicone adhesives cross-linked by Pt-catalyzed hydrosilylation.

With Pt-cured adhesives, the development of adhesion to a substrate often requires a higher temperature or longer times than needed simply to cross-link the adhesive. For more efficient processing, it is obviously desirable to understand and ultimately minimize this thermal offset between curing and adhesion. Because the adhesion is highly dependent on cure temperature, XPS analysis along the gradient allows one to test how interface composition changes as the mode of failure switches from interfacial to cohesive. This method yields new insights into the mechanism of adhesion and provides direct evidence of adhesion promoter reactivity.

An unmodified PDMS elastomer (u-PDMS) is prepared by mixing 56% (w/w) dimethylvinylsiloxy-terminated PDMS (PDMS-Vi), 42% untreated silica filler, 2% PDMS-*ran*-poly(methylhydrogensiloxane) copolymer (PDMS−MH), and 0.2% Karstedt's Pt catalyst dispersed in PDMS. A model silicone adhesive (MSA) is formulated from the control formulation by adding 4% of the organotitanate adhesion promoter[19] (OTAP) shown in Figure 1. A second formulation (MSA + IEA) also contains 4% OTAP but substitutes a poly(methyl-6,6,6,5,5,4,4-nonafluorohexylsiloxane)-*ran*-poly(methylhydrogen siloxane) co-oligomer, total $M_n = 5000$ g/mol with 25 mol % fluorinated repeat units, as an interfacial enrichment additive (IEA) for 1 wt % of the silicon hydride functional cross-linker in the MSA to maintain constant stoichiometry. In all compositions, the total concentration of elemental Pt is 10 ppm (w/w), and the ratio of total silicon hydride to unsaturated groups is 1.5. Samples are mixed with a Hauschild rotary mixer operating at 3500 rpm and then applied in a 0.76 mm thick film onto clean, optically smooth bisphenol A PC substrates (Hyzod M) for curing.

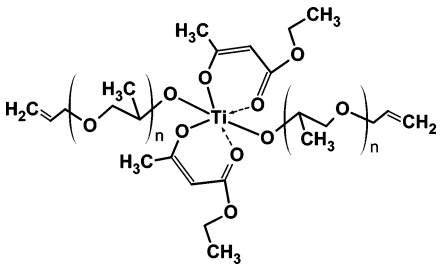

Figure 1. Structure of the OTAP adhesion promoter that is used to internally modify the PDMS in this study, where number average $n = 4$.

Thermal gradient samples for adhesion testing and XPS are heat cured on a thermal gradient press for 30 min at steady state. The temperature ranges from roughly 65 to 140 °C over the length of each sample. Linearity of the gradient is verified by monitoring of embedded thermocouples (Supporting Information). After cooling for 15 min to room temperature, the cured sample is removed from the press and subjected to a 90° static peel test by suspending a 1.5 kg weight attached to the end of a 12.5 mm peel strip cut along the longitudinal center line of the sample. A sharp interfacial crack is created at the low-temperature cure end of the sample using a razor blade. The crack propagates freely along the length of the sample, sampling the interface at a continuously increasing cure temperature, until it arrests where the mode of failure changes from interfacial to 100% cohesive failure in the adhesive. Examining the failure surface on the PC substrate, the position where the crack arrests is measured and converted to the corresponding threshold temperature for cohesive failure (T_{cf}) by using a linear regression fit of the steady-state gradient profile. The PDMS sides of the PDMS/PC interface are then studied by XPS as a function of distance from the end of the cured strip. Further details of the thermal gradient technique and XPS analysis are provided in the Supporting Information.

Linear thermal gradients have been used for high throughput analysis of temperature effects in polymer systems.[20−26] In contrast to studies of viscoelastic effects in pressure sensitive adhesives where the temperature dependence of peeling is studied by conducting the test on a thermal gradient,[22] we probe the development of interface composition as a function of cure temperature in a reactive adhesive by using the thermal gradient only to prepare the sample. The testing is conducted afterward at ambient conditions to decouple viscoelastic effects from the sample's thermal history. The adhesion test results from this methodology are shown in Table 1 for samples with and without OTAP and a sample containing both OTAP and the IEA. These results demonstrate both the necessity of OTAP and the thermal offset between adhesion and curing in this system that provide a basis for the remaining discussion.

The XPS analysis of these samples benefits from structural features of both OTAP and IEA that give distinct contrast from

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Table 1. Thermal Gradient Adhesion Test Results

adhesive sample	wt % OTAP	wt % IEA	T_{cf} (°C)
u-PDMS	0	0	>180
MSA	4	0	105 ± 1
MSA + IEA	4	1	114 ± 1

the silicone matrix. In our system, OTAP is the sole source of Ti and any type of carbon−oxygen bonding (represented nonstructurally as −C−O), while IEA is the exclusive source of fluorocarbon moieties. We use the thermal gradient curing method to probe the transition to cohesive failure asymptotically using XPS. Doing so reveals the temperature dependence of interface composition and permits detection of any trends in interface composition that immediately precede the onset of adhesion.

As shown in Figure 2a,b, analysis of high-resolution C 1s XPS data collected along the gradient reveals distinct maxima in the OTAP contribution to the carbon signal near 80−90 °C for both the MSA and MSA + IEA samples well before adhesion develops. The absolute total carbon concentration varies by 3% or less in each set, and the theoretical contribution of C−O bonding to the C 1s signal for a homogeneous bulk sample containing 4 wt % OTAP is 7.5% (Supporting Information); hence, significant enrichment of OTAP is seen at intermediate cure temperatures, particularly when IEA is present. The ability of IEA to promote interfacial enrichment of OTAP is consistent with our earlier studies with acrylate adhesion promoters.[18] It should be noted that both OTAP and IEA are thermodynamically incompatible in PDMS, but the terminal unsaturation on OTAP, and the silicon hydride on IEA, ensure that both components are reacted into the PDMS via hydrosilylation. This incompatibility leads to strong interfacial segregation, particularly in the presence of IEA. Because of their complementary reactivities, there exists the possibility that OTAP and IEA can react with each other in situ to form a fluorinated adhesion promoter. The extent of OTAP migration is governed ultimately by the balance of diffusivity, time for diffusion, and miscibility and the competing effects of cure temperature thereon.

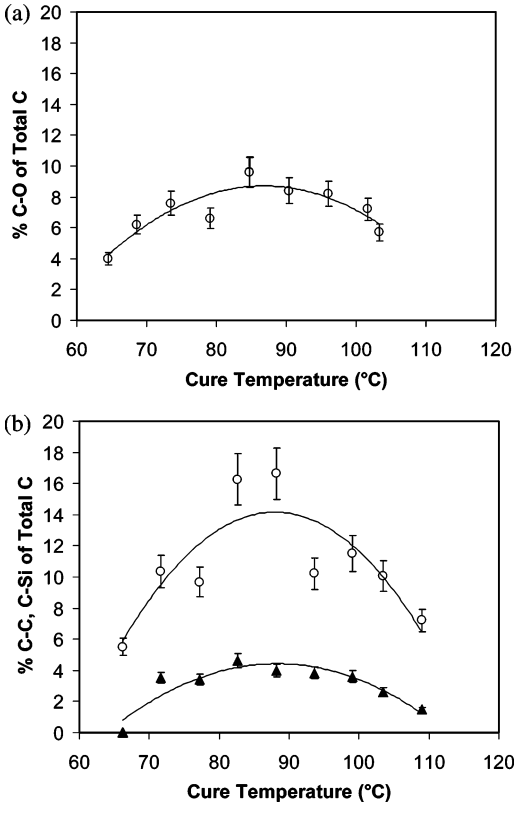

Figure 2. High-resolution C 1s XPS composition profiles as a function of cure temperature history up to the onset of adhesion for (a) MSA and (b) MSA + IEA at the PC interface. Values for carbon oxygen bonding (○, C−O), and carbon−fluorine bonding (▲, C−F) are reported as a percentage of the combined carbon 1s XPS signal. Binomial fits are drawn to guide the eye.

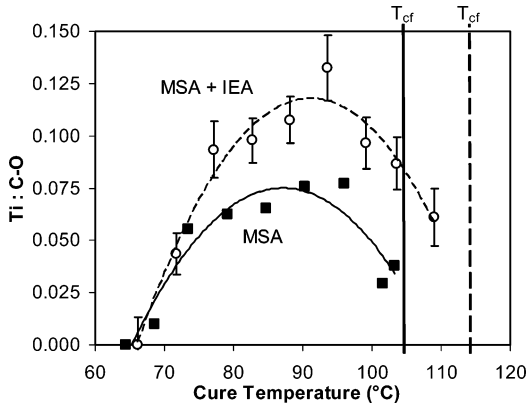

Figure 3. Ratio of elemental Ti from XPS survey spectra to high-resolution C 1s C−O content as a function of cure temperature for MSA and MSA + IEA at the PC interface. The decrease in this ratio that precedes the onset of adhesion (indicated by corresponding lines) in both systems suggests that detachment of the ligands from the Ti center in OTAP may contribute to adhesion. Binomial fits are drawn to guide the eye.

Because the theoretical bulk Ti concentration for a homogeneous sample is only 0.1 at. %, tracking OTAP in the bulk by XPS is difficult. However, the elemental Ti signals are found to be many-fold increased at the maximum due to interfacial enrichment, allowing an internal comparison. The ratio of Ti to C−O signals can provide insight into the fate of the OTAP molecule. If the OTAP structure remains intact at all cure temperatures, the Ti:C−O ratio should remain constant along the gradient. On the contrary, Figure 3 reveals significant curvature in this relationship, suggesting that at least some of the organic ligands on OTAP separate from their Ti center at higher temperatures. In both samples, the onset of cohesive failure (denoted by lines) is preceded by a drop in this ratio. Organotitanates derive their usefulness as catalysts and adhesion promoters from their ability to undergo a variety of ligand exchange reactions. However, the ratios and absolute concentrations of OTAP appear to become closer to their unenriched values as T_{cf} is approached. To this point, our XPS analysis focuses on the PDMS adhesive side of the interface. Subsequent examination of the PC side of the interface near T_{cf} shows no significant Ti signals, while the C−O bonding contributions appear higher than expected for pure PC for both samples, further suggesting that dissociation and migration of ligands from Ti may be occurring. While such relations are expected to be system dependent, the strong correlation between this event and the onset of adhesion in this system encourages further investigation into the mechanism and demonstrates the particular usefulness of coupling temperature gradient based adhesion testing with surface analytical techniques in thermally activated polymer systems.

A high throughput thermal gradient adhesion test methodology has been combined with XPS to correlate titanate adhesion promoter enrichment and reactivity with adhesion in strongly bonded PDMS elastomer−polycarbonate interfaces. For surface analysis techniques, T_{cf} poses a limit to conventional interfacial analysis; the thermal gradient allows one to approach this limit

asymptotically and can reveal trends in interface composition and structure that predict the onset of adhesion. One can extend the thermal gradient analysis beyond the limit of T_{cf} through noninvasive methods for probing buried interfaces, such as sum frequency generation vibrational spectroscopy. The effects of temperature on the substrate side of the interface can also be probed in a high throughput fashion by coupling thermal gradient analysis with compositional imaging of the interfacial cross section. Such efforts are in progress.

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Supporting Information Available: Details of thermal gradient characterization, XPS experiment, and XPS data tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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