tributes to dilation offers a means of unifying the thermodynamic description of gas sorption in low molecular weight solvents, rubbery polymers, and glassy polymers. That is, if account is taken for the amount of unrelaxed volume separating a glassy polymer from a true equilibrium material, it appears that the sorption and dilation behavior of gases in glassy polymers is understandably different from the behavior of gases sorbed into an equilibrium material.

Marked hysteresis is observed in the volume and sorption level for pressurization and depressurization with CO_2 for the case of polycarbonate. This behavior suggests that during depressurization the presence of CO_2 retards relaxation of the polymer to its former thermodynamic state observed during pressurization. These observations are consistent with the behavior reported by others for vapor/polymer systems.

Finally, the unrelaxed volume present in a glassy sample following complete removal of CO_2 appears to be directly assignable to increases in the Langmuir sorption capacity. The unrelaxed volume present in the sample after complete removal of CO_2 correlates very well with an increase in sorption capacity measured for a polymer sample with a similar history.

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Registry No. CO_2, 630-08-0; bisphenol A polycarbonate (SRU), 24936-68-3; (bisphenol A)·(carbonic acid) (copolymer), 25037-45-0.

Supplementary Material Available: Appendix detailing the effect of volume correction on sorption values for carbon dioxide in silicone rubber and polycarbonate (Figures A-1 and A-2) (5 pages). Ordering information is given on any current masthead page.

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Location of the Adhesion Promoter (γ-Aminopropyl)trimethoxysilane in a Cured Silicone RTV Matrix

J. Stein,* S. J. Valenty,* G. A. Smith, D. V. Brezniak, and L. C. Prutzman

General Electric Company, Corporate Research and Development,
Schenectady, New York 12301. Received April 14, 1986

ABSTRACT: Secondary ion mass spectrometry (SIMS) depth profiling has been used to determine the location of (γ-aminopropyl)trimethoxysilane (GAP) in both silica-filled and unfilled silicone RTV elastomers. The adhesion promoter, $NH_2CD_2CH_xD_{2-x}CH_2Si(OMe)_3$, was found to be uniformly distributed throughout the matrix with no apparent increase at either the air– or metal–substrate interface. No adhesion was found in materials without adhesion promoters, which suggests that a minimum concentration at the surface is necessary for adhesion; however, this concentration is not greater than that found in the bulk.

A typical RTV composition contains reactive end-stopped polymer, cross-linker, filler, catalyst, and adhesion promoter. In most cases, the adhesion promoter is an organofunctional trialkoxysilane such as (methacryloxopropyl)trimethoxysilane or (aminopropyl)trimethoxysilane. Unfortunately, the mechanism of adhesion to substrates induced by these silanes is poorly understood. Two roles for the adhesion promoter may be envisioned. First, the molecule may interact with both the substrate and the matrix to form either a chemical or physical linkage between them. Alternatively, the adhesion promoter may alter the polymer morphology, thereby producing a material with greater intrinsic adhesion. Of course, the role may be a combination of the two effects.

In order to more clearly define the mechanistic aspects of adhesion, we decided to determine the location of the adhesion promoter in RTV's by using the SIMS depth-profiling technique. One would assume that if chemical linkages or strong physical interactions between the elastomer and the substrate were necessary, an appreciable concentration of the adhesion promoter would be found at the interface. Furthermore, depth profiling would determine whether a concentration gradient exists at the interface.

As an analytical technique, SIMS is unsurpassed in its ability to detect a wide range of elements (hydrogen to uranium) at high sensitivity (ppb to ppm atomic) and provide three-dimensional mapping of elemental composition.[1] The interaction of a 5–20-keV ion beam with a surface removes, or sputters, species characteristic of that material, e.g., neutral and charged atoms and molecular fragments as well as electrons and photons. SIMS involves a mass spectrometric analysis of these positive and negative atomic and molecular fragments. By monitoring one or more of these secondary ions as material is removed, one may obtain an in-depth analysis of the sample. The key to the profiling capability of SIMS is its shallow sampling depth, ca. 5–50 Å.

While SIMS has found widespread application in inorganic solid-state and semiconductor research,[2] a relatively small number of papers have involved analyses of organic and biological materials.[3] In most of these cases, "static" SIMS (low primary beam current density and energy) has been employed to detect molecular fragments from only the outermost monolayer(s) in order to obtain "fingerprint" mass spectra useful for characterizing the organic substrate. The lateral imaging capabilities of static SIMS have been recently demonstrated on organic surfaces by Briggs.[4] Fewer cases have been reported for "dynamic" SIMS (higher primary beam energies and current densities) in which depth profiling of organic polymeric matrices is desired. DiBenedetto and Scola[5] used SIMS to depth profile an incompletely cured silane coating on glass. The SIMS spectra at different depths of penetration revealed that three interphase domains exist, each differing in the concentration of nitrogen and hydrogen present, within a depth of 250 Å from the glass silane interface.

We report SIMS in-depth profiling of a deuterated small molecule in a silicone matrix over distances of several micrometers. The advantages of using deuterium labeling are twofold: (1) Deuterium at nominal m/e 2 is essentially free of any matrix interferences from the organic materials being studied; in fact, the limit of detection is governed by the natural isotopic abundance of deuterium found in the polymer. The relatively low secondary ion yield for H_2^- and the use of a mass-analyzed primary ion beam to reduce beam contaminants further aid in providing a high signal-to-noise ratio for deuterium detection. (2) As for many other labeling applications incorporating deuterium, little perturbation of the chemical system is expected by substituting deuterium for hydrogen. Hence, the rate of diffusion of a relatively large molecule with low deuterium content through a polymeric matrix will be the same as that of the hydrogen analogue.

Both silica-filled and unfilled model RTV formulations were prepared which incorporated $H_2NCD_2CH_xD_{2-x}CH_2Si(OMe)_3$ (GAP-d_3) as adhesion promoter. RTV formulations contained ~1.0 wt % adhesion promoter. SIMS test specimens were prepared by coating a gold coupon with a thin film (<1 mm thick) of RTV, which was then cured for one week prior to analysis. A 300–500-Å gold overlayer was evaporated on the front face of the RTV sample to minimize charging of the sample surface region during ion bombardment.

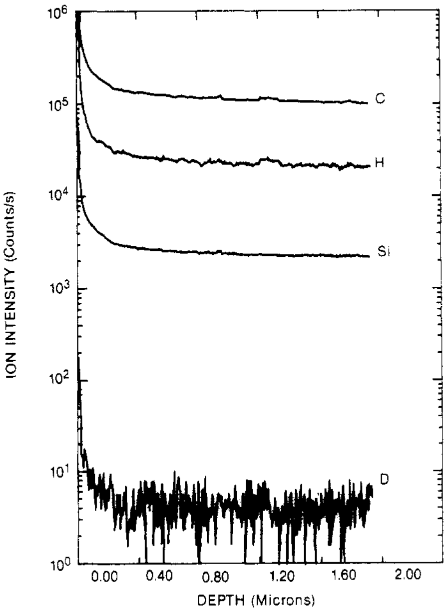

Figure 1. Depth profile of filled RTV with no GAP-d_3.

A Cameca IMS-3f ion microscope was used to obtain depth profiles. Data were accumulated with a mass-analyzed primary beam of $^{16}O^-$ having an impact energy of 5.5 keV and a current density of ca. 3.5 mA/cm^2.

The intensities of negative secondary ions were measured. The pressure in the sample chamber during analysis was (2–3) × 10^{-8} torr. The primary beam was rastered over an area of ~250 × ~250 μm with an analyzed area of 60-μm diameter as limited by the secondary ion optics. Sputtering rates of ca. 5 Å/s were obtained by ratioing the depth of each crater as measured by a profilometer to the total profile time. Analysis profiles ranged from 3 to 40 μm.

The depth profiles of C, H, Si, and D for an RTV which has not been enriched in deuterium are shown in Figure 1. It is apparent that the elemental composition remains constant throughout the profile. The observed D/H ratio, ~1.5 × 10^{-4}, is equal to the ratio one would calculate based on the isotopic abundance of deuterium in hydrogen.

Elemental depth profiles of cured, silica-filled RTV's containing $NH_2CD_2CH_xD_{2-x}CH_2Si(OMe)_3$ (GAP-d_3) were obtained by profiling through the air–RTV interface. The RTV was then peeled away from a gold-coated copper substrate, and depth profiles from the RTV/metal into RTV and RTV/metal into metal interfaces were obtained (Figure 5). In all three cases, the D/H ratio remains constant throughout the profile at approximately (7–9) × 10^{-4} indicating that no preferential migration to any interface has occurred (Figure 2a). However, since the silica filler, with a surface area of ca. 200 m^2/g, provides the largest accessible surface to the adhesion promoter, one may hypothesize that the adhesion promoter might preferentially sorb onto the filler. In order to determine whether the presence of filler was perturbing the results, a formulation which contained no filler but did contain GAP-d_3 was analyzed. In this case, however, the unfilled RTV was allowed to cure on a gold-coated copper coupon,

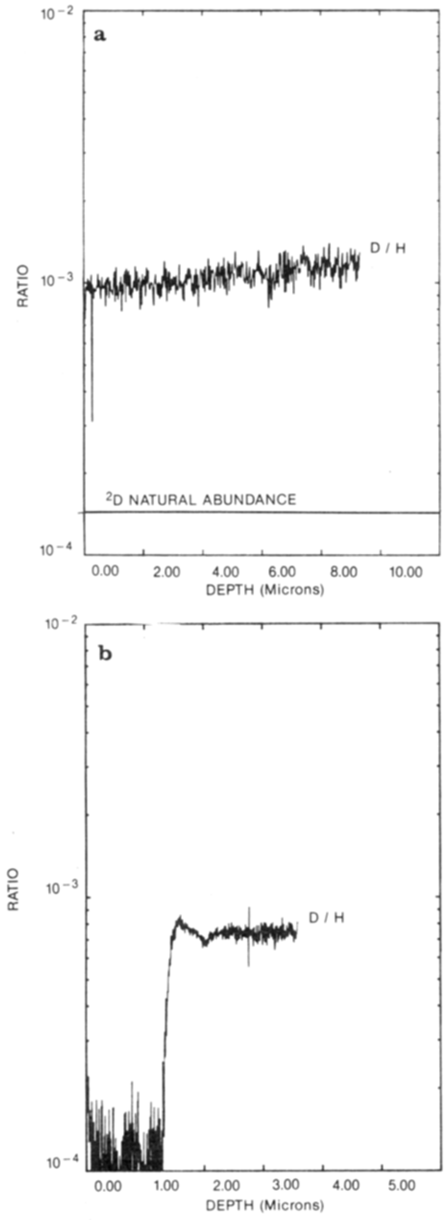

Figure 2. (a) D/H ratio of filled RTV with GAP-d_3. (b) D/H ratio of unfilled RTV with GAP-d_3. Metal/RTV into RTV interface.

and the gold was easily removed from the copper (Figure 5). The sample was then profiled through the gold into the RTV.

The results of the above experiment are shown in Figure 2b. There is no deuterium at the metal–RTV interface until the gold has been sputtered away. Again, it is apparent that no D/H concentration gradients are present either in the matrix or at either interface, indicative of uniform dispersion of the adhesion promoter throughout the matrix.

In order to test whether these results are a function of surface saturation of the adhesion promoter on the RTV surface, an RTV with no deuterated constituents was prepared and allowed to cure on the gold coupon for 1 week. GAP-d_3 was then topically applied to the surface and allowed to diffuse into the matrix, and the sample was subsequently analyzed. The results are shown in Figure 3. Clearly a gradient exists, and the surface D/H ratio is less than that found in the labeled molecule itself whereas the internal D/H ratio is more similar to that found in the labeled RTV. Thus our labeled RTV's are not surface saturated (only GAP-d_3 on surface) with GAP-d_3 since we would expect a D/H ratio at the surface equal to that found in unhydrolyzed GAP-d_3 itself or higher if this were the case. Artifacts of the SIMS experiment may place limitations on the interpretation of these elemental depth profiles. Loss of depth resolution with increasing sputtering depth is certain. Optical micrographs of the SIMS crater are shown in Figure 4. The sides of the crater are clearly defined. However, extensive beam damage of the crater is evident since cracking and

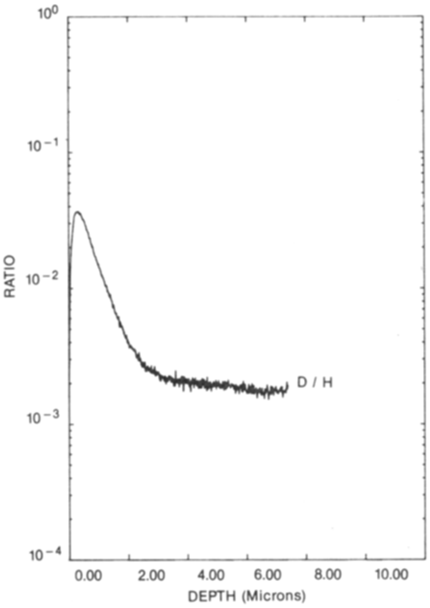

Figure 3. D/H ratio of cured RTV with surface layer of GAP-d_3.

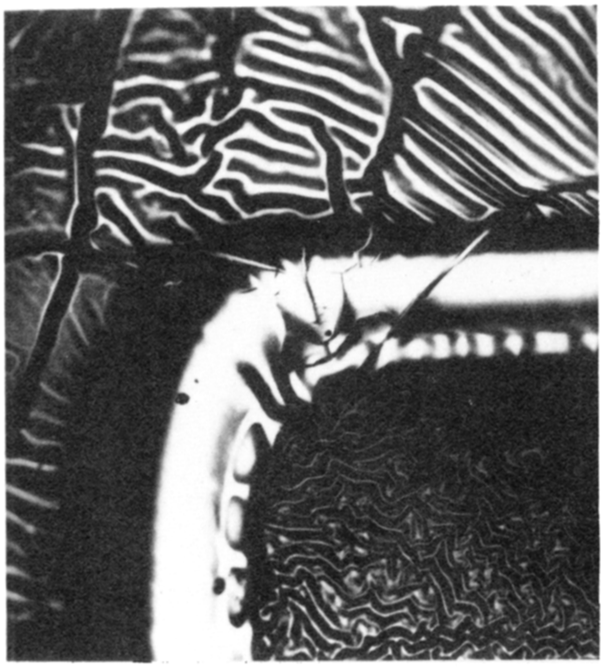

Figure 4. Optical micrograph of SIMS crater.

Table I
Elemental Composition of RTV Surfaces

sample	% C	% O	% Si
filled RTV			
SIMS crater	48	24	22
unsputtered	48	25	25
unfilled RTV			
SIMS crater	51	23	26
unsputtered	49	21	28

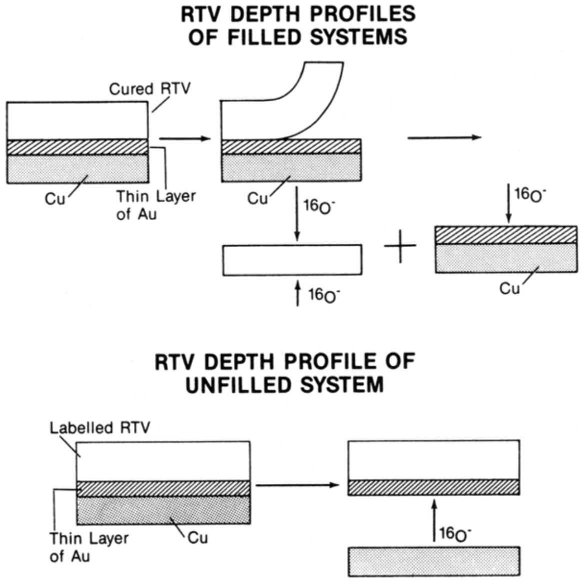

Figure 5. Depth profiles of cured RTV's.

rough microtopography are seen. Pictures of unfilled systems are similar.

The results of small-spot ESCA of the crater floor are presented in Table I. The data in Table I show only slight compositional differences between the SIMS crater and unsputtered silicone RTV's. Gold is no longer present in the sputtered area. In addition, tin was detected on the floor of the crater. Tin is present in the RTV cure catalyst. The chemistry of carbon and oxygen appears to be unchanged by the ion beam. This was evidenced in the C(1s) and O(1s) spectra, which showed no differences between the SIMS crater and unsputtered RTV's. However, the silicon peak of the silicon in the crater may have shifted to higher binding energy by about 0.5 eV. This feature may be due to an oxidized form of Si, most likely SiO_2 from the filler.

The ESCA results obtained with the unfilled RTV are similar. Normally, the compositional ratios are 50% C, 25% O, and 25% Si and the unfilled crater ratios are 51% C, 23% O, and 26% Si, indicating little compositional change upon sputtering.

We have shown that GAP, formulated into a silicone RTV before cure, is found at the air/RTV and RTV/metal surface. Furthermore, this molecule is uniformly distributed throughout both filled and unfilled RTV matrices and does not preferentially segregate in the interphase regions. These data complement results from RTV adhesion testing which indicate a minimum amount of adhesion promoter is necessary to provide adequate peel strength.[6] The exact nature by which GAP then modifies the RTV–substrate interface to achieve adhesion is not known and requires further attention. Whether GAP also acts to change the structure of the cross-linked elastomeric network is also unclear.

SIMS continues to be a valuable tool to employ when attempting to locate small molecules in polymeric matrices. Continued effort must be maintained to determine how the ion beam–polymer interaction affects the interpretation of the analytical data obtained.

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Registry No. GAP-d_3, 102922-78-1.

Supplementary Material Available: Synthesis and characterization data for $NH_2CD_2CH_xD_{2-x}CH_2Si(OMe)_3$ (2 pages). Ordering information is given on any current masthead page.

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