Molecular Structures of the Buried Interfaces between Silicone Elastomer and Silane Adhesion Promoters Probed by Sum Frequency Generation Vibrational Spectroscopy and Molecular Dynamics Simulations

Anne V. Vázquez,[†] **Andrew P. Boughton,**[†] **Nick E. Shephard,**[‡] **Susan M. Rhodes,**[‡] **and Zhan Chen**[*,†]

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109, and Dow Corning Corporation, Midland, Michigan 48686

ABSTRACT Silane adhesion promoters are commonly used to enhance the adhesion of elastomeric materials to polymers in many industrial applications. However, it is difficult to study the molecular-level mechanisms underlying adhesion promotion because adhesion occurs at the boundary between two layers, a buried interface that is difficult to probe with most techniques. Here, a surface/interface-sensitive optical technique, sum frequency generation vibrational spectroscopy, was used to probe the buried interfaces between the silicone elastomer and (3-glycidoxypropyl)trimethoxysilane (γ-GPS) as well as a known silane adhesion-promoting mixture of γ-GPS and methylvinylsiloxane (MVS). The γ-GPS methoxy groups were found to order at the silicone interface both in the neat silane and in the mixture with MVS. The interfacial structures between the silicone elastomer and two other silanes not used as adhesion promoters, *n*-octadecyltrimethoxysilane (OTMS) and (tridecafluoro-1,1,2,2-tetrahydrooctyl)trimethoxysilane (TDFTMS), and their mixtures with MVS, were also compared to those of γ-GPS and the γ-GPS/MVS mixture. It was found that these silanes behaved differently than the known adhesion-promoting mixture. Further, molecular dynamics simulations confirmed that all silanes showed broad, random orientation distributions at the silicone interface. Because only the known adhesion-promoting mixture of γ-GPS and MVS exhibited methoxy order at the silicone interface, as well as at the poly(ethylene terephthalate) interface, as shown in a previous publication, it is inferred that this ordering may be a necessary condition for adhesion promotion.

KEYWORDS: sum frequency generation vibrational spectroscopy • polymer adhesion • polymer interfaces • silicone elastomer • silane adhesion promoters • molecular dynamics simulations

I. INTRODUCTION

Silicone elastomer adhesives are widely used in many applications in the electronics, automotive, and aviation fields as a less expensive alternative to mechanical fasteners. In particular, addition-cured silicones are valuable as adhesives for their high thermal stability, unique rheological properties, and simple, controllable cure chemistry (1−4). However, the addition-curing process leaves these elastomers without intrinsic functional groups that allow for easy adhesion to other polymeric materials. Often, corona or plasma pretreatments are used to alter the surface of the substrate to improve adhesion, but these are both expensive and time-consuming in industrial processes.

To avoid the need for pretreatments, adhesion promoters are often used to improve the adhesion between elastomers and substrates. Many organosilane adhesion promoters have been developed to adhere elastomers to a variety of metal, inorganic, and organic materials. Specifically, alkoxysilane adhesion promoters have been developed to enhance the adhesion of elastomers to other polymers. Small amounts of silane adhesion promoters can be mixed with the silicone elastomer prior to application to the substrate and cure, or silane adhesion promoters can be used as an interlayer between the substrate and elastomer (3, 5−11). It can be assumed that silane adhesion promoters largely work by mechanisms at the interface between the substrate and the elastomer. However, such interfacial mechanisms are extremely difficult to study. Strong adhesive bonds form buried interfaces that cannot easily be broken for examination by surface-sensitive analytical techniques. Further, even if an adhesive bond could be broken and the two resulting surfaces could be examined, breaking the interface may chemically alter the two surfaces and not accurately reflect the interfacial chemistry of the adhesive bond. Therefore, to study interfaces involved in adhesion, a technique that can probe buried interfaces must be employed.

---

[*] E-mail: zhanc@umich.edu.

Received for review September 10, 2009 and accepted December 5, 2009

[†] University of Michigan.

[‡] Dow Corning Corporation.

DOI: 10.1021/am900612r

Sum frequency generation (SFG) vibrational spectroscopy is a second-order nonlinear optical technique that is sensitive to surfaces and buried interfaces that are accessible by light (12−16). SFG can detect the presence, coverage, and orientational ordering of surface or interfacial chemical groups *in situ*. SFG has been extensively used to study polymer surfaces and interfaces, including polymer/air interfaces, polymer surface restructuring in water, the surface structure of polymer blends and copolymers, polymer/biomolecule interfaces, polymer/silane interfaces, and polymer/silicone elastomer interfaces (17−38).

It has been demonstrated that a silane adhesion-promoting mixture of organosilane and siloxanol can greatly improve the adhesion between addition-cured silicone elastomers and polymer substrates. Specifically, a mixture of (3-glycidoxypropyl)trimethoxysilane (γ-GPS) and methylvinylsiloxane (MVS) has been shown to promote adhesion between poly(butylene terephthalate) (PBT) and addition-cured silicone elastomer. Alone, neither γ-GPS nor MVS improves adhesion. However, when only a very small amount of the silane adhesion-promoting mixture is incorporated into the silicone elastomer prior to application to PBT and curing, adhesion is improved dramatically (10, 11).

SFG has previously been used to study interactions between the silane adhesion-promoting mixture and poly(ethylene terephthalate) (PET), a polymer analogous to PBT. In SFG studies of PET in contact with γ-GPS and the silane adhesion-promoting mixture of γ-GPS and MVS, it was found that the γ-GPS methoxy groups order at the PET/γ-GPS interface and that the ordering of the γ-GPS methoxy groups is increased when it is mixed with MVS (18). When compared to two other silanes not used as adhesion promoters (and their mixtures with MVS), it was found that the other silanes exhibited different interfacial behavior (37). This indicated that the increased ordering of the γ-GPS methoxy groups when mixed with MVS may be a necessary condition for adhesion promotion. Further, SFG studies of PET/silicone elastomer interfaces with incorporated γ-GPS or the silane adhesion-promoting mixture of γ-GPS and MVS were conducted. Two other silanes not used as adhesion promoters (and their mixtures with MVS) were also used in these studies for comparison (37). It was found that only the γ-GPS methoxy groups ordered at the interface when mixed with MVS in the silane adhesion-promoting mixture both before and after the silicone was cured. Because the other silanes (alone or mixed with MVS) did not exhibit this behavior, it was concluded that the ordering of the γ-GPS methoxy groups at the PET/silicone elastomer interface both before and after cure is necessary for adhesion promotion in this system (37).

While earlier research has focused on the interactions between the polymer substrate and adhesion promoter, interactions between the silicone elastomer and adhesion promoter may also play an important role in the ability of a silane or silane mixture to enhance adhesion between a polymeric substrate and a silicone elastomer. This is true both when the adhesion promoter is incorporated into the silicone elastomer prior to cure and also when the adhesion promoter is used as an interlayer between the substrate and elastomer. In the present study, the interfaces between an addition-cured silicone elastomer and γ-GPS, as well as the silane adhesion-promoting mixture of γ-GPS and MVS, were investigated with SFG. The interfacial structures of two other silanes not used as adhesion promoters, *n*-octadecyltrimethoxysilane and (tridecafluoro-1,1,2,2-tetrahydrooctyl)-trimethoxysilane, and their mixtures with MVS, were also investigated at the silicone elastomer interface for comparison. Molecular dynamics (MD) simulations were performed to calculate the orientation of the silane methoxy groups at the silicone interface to supplement the SFG results. MD results were used to determine if the silanes exhibited a narrow or broad orientation distribution at the silicone interface.

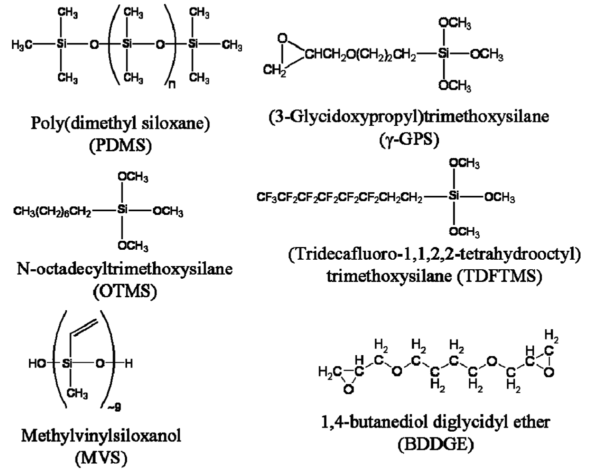

FIGURE 1. Structures of the silicone elastomer, silanes, MVS, and BDDGE.

II. EXPERIMENTAL SECTION

1. Materials. A Sylgard 184 silicone elastomer kit, (3-glycidoxypropyl)trimethoxysilane (γ-GPS) and methylvinylsiloxane (MVS), were obtained from Dow Corning Corporation. The other two silanes, *n*-octadecyltrimethoxysilane (OTMS) and (tridecafluoro-1,1,2,2-tetrahydrooctyl)trimethoxysilane (TDFTMS), were obtained from Gelest. The Sylgard 184 silicone elastomer was prepared in a 10:1 (wt/wt) base/curing agent ratio. The elastomer base and curing agent were mixed vigorously to the point of visual homogeneity and were diluted to a 5 wt % solution in toluene. Thin films of the silicone elastomer were prepared by spin-casting the diluted solution onto fused silica windows purchased from ESCO Products (1 in. diameter and $^{1}/_{8}$ in. thickness) using a spin coater from Specialty Coating Systems. The silicone elastomer thin films were cured at 150 °C for 1 h prior to analysis. The silanes were used as received. When the silanes were mixed with MVS, the following solutions were prepared: 1:1 (wt/wt) γ-GPS/MVS, 1:1 (w/w) OTMS/MVS, and 2:1 (wt/wt) TDFTMS/MVS. The solutions were mixed to the point of visual homogeneity. To compare the signal of the epoxy-functionalized silane γ-GPS to that of a different sample with epoxy groups, a thin film of 1,4-butanediol diglycidyl ether (BDDGE) was spin-cast from a 1 wt % solution in chloroform onto a fused silica window for SFG analysis. The structures of the silicone [poly(dimethylsiloxane) (PDMS)], silanes, MVS, and BDDGE are shown in Figure 1.

2. SFG Experiments. SFG theory has been well-developed and reported in the literature (12−16). Further, the experimental geometry used in these experiments has been detailed in previous publications (18, 20, 22−24). Briefly, a fixed-frequency visible beam and a frequency-tunable IR beam are overlapped spatially and temporally at the polymer/liquid interface at 60° and 54°, respectively, with a beam diameter of approximately 500 μm. The visible and IR energies are approximately 100 and 200 μJ, respectively. Previous results have shown that the SFG signal is dominated by the signal from the polymer/liquid interface rather than that from the polymer bulk or the polymer/substrate interface (18, 22, 23). In the current investigation, all spectra were obtained in the ssp (s-polarized SFG signal, s-polarized visible light, and p-polarized IR light) polarization combination. Other polarization combinations did not yield a discernible signal.

3. MD Simulations. MD simulations were carried out using Materials Studio 4.3 (Accelyrs, Inc.), using the Amorphous Cell (AC) and Forcite modules. NVT MD simulations were run at 298 K using the Anderson thermostat. The COMPASS force field, a class II force field optimized for condensed-phase simulations, was used for all calculations (39). The AC module was used to simulate a 17-monomer chain of vinyl-terminated PDMS with periodic boundaries. The AC module was also used to make periodic cells of 16 molecules of γ-GPS, a 1:1 γ-GPS/MVS (8 molecules of γ-GPS and 8 molecules of MVS) mixture, OTMS, and TDFTMS. All periodic cells had a cutoff size of 12.5 Å. Each cell was equilibrated in the following manner. An initial geometric optimization was performed using the conjugate gradient method with a root-mean-square (rms) atomic force cutoff of 0.1 kcal/mol · Å, followed by 50 ps NVT MD at 298 K with a 1 fs time step using the Velocity Verlet algorithm and the COMPASS force field. The 50 ps simulation time was sufficient for the potential energy to equilibrate, consistent with other reported polymer simulations of this nature (40). Longer simulations were run with similar results for some of the silanes and some of the silicone/silane interfaces (not shown). The cells were then subjected to a second geometric optimization using the conjugate gradient method with an rms atomic force cutoff of 0.01 kcal/mol · Å (40, 41). Interfaces were simulated using the Layer Builder Tool to create two-dimensional periodic systems. The interfaces were equilibrated in the same manner as that described above.

The equilibrium orientation angle distribution of the silane methoxy groups was calculated for each silane studied. The coordinates of a single final trajectory frame were analyzed from five different simulations for each system studied. The final results from the multiple simulations of each system (using different initial random seed values) were consistent across all similar trajectories. The angle distributions of the individual CH_3 groups of the silane trimethoxy groups were calculated with respect to the surface normal of the plane of the silicone/silane (or silane mixture) interface. A correction factor was included to remove the bias resulting from variations in the solid angle (42).

III. RESULTS AND DISCUSSION

1. SFG Studies of the Silicone Elastomer in Contact with Neat γ-GPS and the γ-GPS/MVS Mixture. SFG spectra were taken of cured silicone elastomers in contact with neat silanes and the silane mixtures with MVS. Spectra were obtained immediately upon contact between the silicone elastomer and silane (or silane mixture). The laser was then blocked for 15 min to allow the system to equilibrate, and a spectrum was obtained again. This procedure was repeated every 15 min for a total of 60 min (not shown). No spectral changes were observed after 30 min for any of the systems studied, so only spectra taken within 30 min are reported.

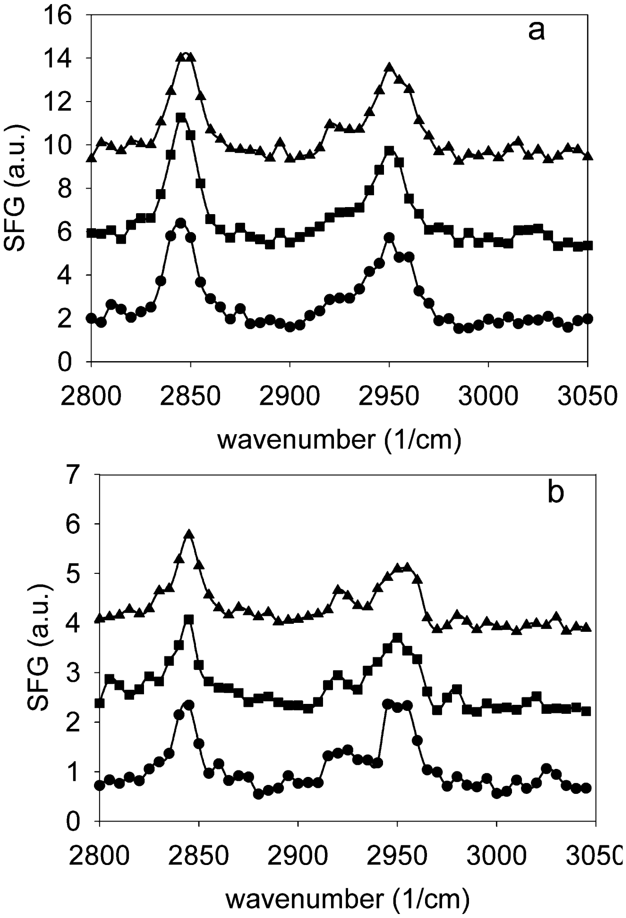

FIGURE 2. (a) SFG spectra of silicone in contact with γ-GPS at the initial contact (circles), 15 min after contact (squares), and 30 min after contact (triangles). (b) SFG spectra of silicone in contact with the γ-GPS/MVS mixture at the initial contact (circles), 15 min after contact (squares), and 30 min after contact (triangles). Spectra are offset.

SFG spectra of cured silicone elastomers in contact with γ-GPS and the γ-GPS/MVS mixture over 30 min are shown in Figure 2. In the spectra of silicone in contact with γ-GPS, a peak was observed at 2840 cm^{-1}, which was stable over 30 min. This peak is characteristic of the γ-GPS methoxy symmetric stretch (18). The stable intensity indicates that the interface between silicone and γ-GPS was stable with time. The silane signal was only obtained from the ssp polarization combination, meaning that the γ-GPS methoxy groups were most likely ordered at the silicone interface with a broad interfacial orientation distribution. This interpretation agrees with the MD simulation results, which indicated a broad angle distribution, as will be discussed below. Also, a stable silicone signal was observed. A larger peak at 2960 cm^{-1} and a smaller peak at 2910 cm^{-1} were attributed to the PDMS asymmetric and symmetric methyl stretches, respectively (25). This shows that the silicone methyl groups were ordered at the silicone/γ-GPS interface.

SFG spectra of silicone in contact with the 1:1 γ-GPS/MVS mixture are also seen in Figure 2. Here, a stable peak at 2840 cm^{-1} from the γ-GPS methoxy symmetric stretch was also detected. Like neat γ-GPS, the γ-GPS methoxy groups ordered at the interface, most likely with a broad orientation distribution, as confirmed by MD simulation results. However, the silane signal was slightly weaker than that from the interface between silicone and neat γ-GPS. This contrasts with the silane signal from the interface between PET and γ-GPS and the 1:1 γ-GPS/MVS mixture. We believe that the different SFG signal intensities are not due to the refractive index differences because neat γ-GPS and the γ-GPS/MVS mixture have very similar refractive indices. Such signal differences must be caused by varied interfacial structures and coverages. At the PET interface, the signal from γ-GPS was stronger when mixed with MVS, indicating that MVS acted to order γ-GPS at that interface (18, 37). At the silicone elastomer interface, MVS may have acted to slightly disorder the γ-GPS methoxy groups, which would result in a decrease in the signal. Another possible explanation is that MVS preferentially interacted with silicone and therefore diluted γ-GPS at the interface. Because SFG is sensitive to the interfacial number density, this dilution effect would lower the SFG signal. Additionally, a stable peak at 2960 cm^{-1} with a shoulder at 2910 cm^{-1} was attributed to the silicone elastomer, possibly with some contribution from MVS (37). The silicone signal at the γ-GPS/MVS mixture interface was similar to that at the neat γ-GPS interface, indicating that the silicone methyl groups adopted a similar interfacial orientation.

It is important to note that other functional groups that could be involved with adhesion promotion were present in this system, namely, the epoxy groups from γ-GPS and the vinyl groups from MVS. Because both groups could participate in the silicone cross-linking, it may be expected for these groups to order at the silicone interface. However, no discernible signal from either the epoxy groups or the vinyl groups was observed. The lack of a vinyl signal may be due to two different factors. First, the vinyl signal from MVS may have been present but may not have been discernible from the silicone signal. Another possibility is that because the silicone elastomer was cured prior to contact with the silane mixture, the MVS vinyl groups may not be attracted to the cross-linked silicone surface. The groups therefore would not preferentially order at the interface, and no SFG signal would be observed.

The lack of a epoxy signal from the γ-GPS silane may also be due to a variety of factors. For comparison, Figure 3 shows an SFG spectrum of a thin film of BDDGE, an epoxy-containing compound. In this spectrum, among other C—H stretches, the C—H stretching mode of the epoxy ring is seen at 3000 cm^{-1} (43). Here, because the spin-cast BDDGE thin film has an ordered surface, the epoxy ring C—H stretch is visible in the SFG spectrum, showing that it is possible to obtain a SFG epoxy ring C—H signal in the C—H stretching region. However, this epoxy signal was not observed at the buried interface between the silicone elastomer and γ-GPS (or the γ-GPS/MVS mixture). Therefore, the epoxy rings were either not present at the interface, or they were present but not ordered at the interface. Because it was observed that the γ-GPS methoxy groups were ordered at the interface with a broad angular distribution, it is most likely that the γ-GPS epoxy groups were not well-ordered at the interface. The interface between the silicone elastomer and γ-GPS is therefore dominated by the more ordered γ-GPS methoxy groups. As described above, it is possible that the γ-GPS epoxy groups did not strongly order at the silicone interface because silicone was cross-linked prior to contact with silane (or the silane mixture).

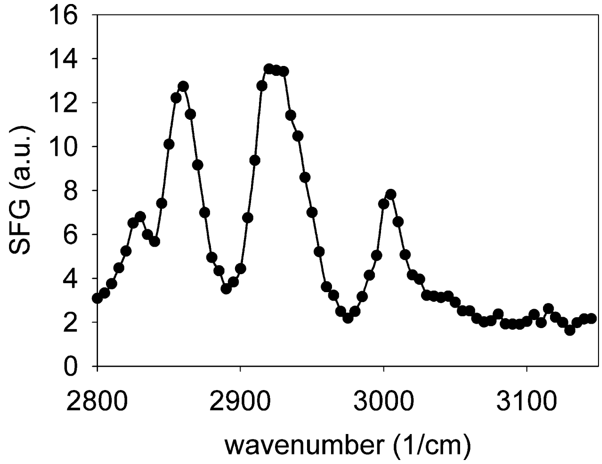

FIGURE 3. SFG spectrum of BDDGE.

In summary, SFG spectra of silicone elastomer in contact with γ-GPS and the γ-GPS/MVS mixture showed that a stable interface was formed with the γ-GPS methoxy groups ordered at the interface. Because only ssp signal was obtained, it was inferred that the interfacial methoxy groups most likely had a broad orientation distribution. This was confirmed by MD simulations, which will be discussed below. Further, no evidence of the γ-GPS epoxy groups ordering at the interface was observed. The γ-GPS methoxy signal was slightly weaker when mixed with MVS. This decrease in the SFG signal may have been because MVS acted to disorder γ-GPS at the silicone interface. The lower signal may also have been due to dilution effects. MVS may have preferentially interacted with the silicone surface, dominating the interface and therefore lowering the γ-GPS signal. Unfortunately, SFG cannot be used to distinguish between these two possibilities.

2. SFG Studies of the Silicone Elastomer in Contact with Neat OTMS and the OTMS/MVS Mixture. As discussed previously, the γ-GPS/MVS mixture is a known silane adhesion-promoting mixture for silicone elastomer adhesion to PBT and PET. To understand why this is such an effective adhesion promoter, it is important to understand how MVS affects the interfacial behavior of γ-GPS, as was discussed above. It is also necessary to compare the known silane adhesion-promoting mixture to other silanes that do not act as adhesion promoters, as well as their mixtures with MVS, to determine if the interfacial behavior of γ-GPS and the γ-GPS/MVS mixture is unique to the adhesion-promoting mixture or if it is universal to all silanes. Here, two other trimethoxysilanes with different

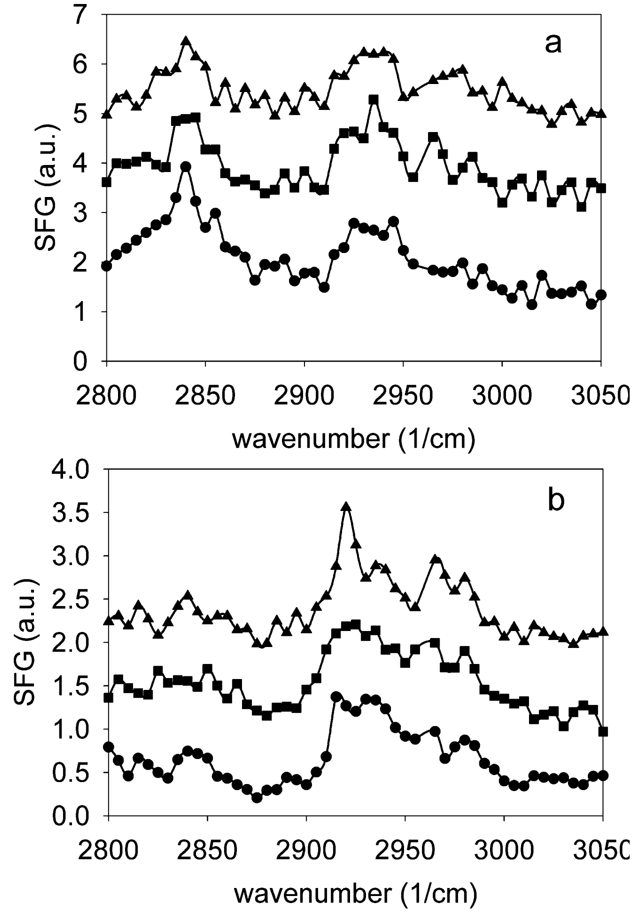

FIGURE 4. (a) SFG spectra of silicone in contact with OTMS at the initial contact (circles), 15 min after contact (squares), and 30 min after contact (triangles). (b) SFG spectra of silicone in contact with the OTMS/MVS mixture at the initial contact (circles), 15 min after contact (squares), and 30 min after contact (triangles). Spectra are offset.

backbones were investigated for comparison. OTMS has a methylene backbone, while TDFTMS has a fluoroalkyl backbone.

SFG spectra of the silicone elastomer in contact with OTMS and the OTMS/MVS mixture are shown in Figure 4. For silicone in contact with OTMS, the weak stable signal at 2840 cm^{-1} was attributed to the OTMS methoxy symmetric stretch. The weak signal only in the ssp polarization combination indicated that the OTMS methoxy groups were present at the interface but were weakly ordered. The broad orientation distribution of the OTMS methoxy groups was confirmed by MD simulations, as shown below. Also, the stable SFG signal at 2960 cm^{-1} was attributed to the silicone elastomer. The silane signal from OTMS was weaker in intensity than that from γ-GPS seen in Figure 2. This may be because OTMS was less ordered at the silicone interface than γ-GPS. Specific interactions between the silicone surface and γ-GPS may have caused γ-GPS to exhibit stronger order.

SFG spectra of the silicone elastomer in contact with the OTMS/MVS mixture, seen in Figure 4, showed no indication of the OTMS methoxy groups ordering at the silicone interface, as evidenced by the lack of a signal at 2840 cm^{-1}. There were, however, stable signals at 2910 and 2960 cm^{-1}, attributed to the silicone elastomer and/or MVS. The lack of a signal from the OTMS methoxy groups may have been due to two different reasons. First, MVS may have acted to disorder OTMS at the silicone interface. If MVS caused OTMS to become disordered at the silicone interface, the signal would be lost. Second, MVS may have preferentially interacted with silicone. If MVS had significantly stronger interactions with silicone than OTMS, in the mixture, MVS may cover the silicone interface and block OTMS from reaching the interface. This would cause the OTMS signal to be lost. Again, because no specific signal from MVS can be distinguished, SFG cannot be used to differentiate between these two possibilities.

SFG spectra of silicone in contact with OTMS and the OTMS/MVS mixture were quite different from those of silicone in contact with γ-GPS and the γ-GPS/MVS mixture. The OTMS methoxy groups were less ordered at the silicone interface than those of γ-GPS. Therefore, interactions between silicone and γ-GPS may have been stronger than interactions between silicone and OTMS. At the interface between silicone and the γ-GPS/MVS mixture, the γ-GPS methoxy groups remained ordered even when mixed with MVS, while there was no evidence of the OTMS methoxy groups ordering at the interface between silicone and the OTMS/MVS mixture. As discussed above, this may have been because MVS disordered OTMS or because MVS diluted OTMS at the interface. It is important to note that MVS is necessary for adhesion promotion because the vinyl groups can participate in the cross-linking of the silicone elastomer. Therefore, if a neat silane adopts a specific necessary orientation at the silicone interface, it must maintain that orientation when mixed with MVS to be able to behave as an adhesion promoter. Because γ-GPS remained ordered in the known silane adhesion-promoting mixture of γ-GPS and MVS while OTMS did not remain ordered when mixed with MVS, the ability of the γ-GPS methoxy groups to remain ordered at the silicone interface when mixed with MVS may be a necessary condition for the mixture to act as an adhesion promoter.

3. SFG Studies of Silicone Elastomer in Contact with Neat TDFTMS and the TDFTMS/MVS Mixture. SFG spectra of silicone in contact with neat TDFTMS and the TDFTMS/MVS mixture are shown in Figure 5. SFG spectra of the silicone elastomer in contact with TDFTMS showed a signal at 2840 cm^{-1} from the TDFTMS methoxy groups. The peak was observed immediately upon contact between silicone and silane. The peak intensity decreased after 15 min and then remained stable. The decrease in the peak intensity may have been due to different mechanisms. First, the decrease in the signal may have been because the interface equilibrated more slowly than the other two silane systems. Over 15 min, the system may have equilibrated, causing the TDFTMS methoxy groups to slightly disorder/reorient at the interface. A second explanation is that there may have been a slow diffusion of TDFTMS into the silicone elastomer. As TDFTMS diffused into silicone, the interface would have become less ordered

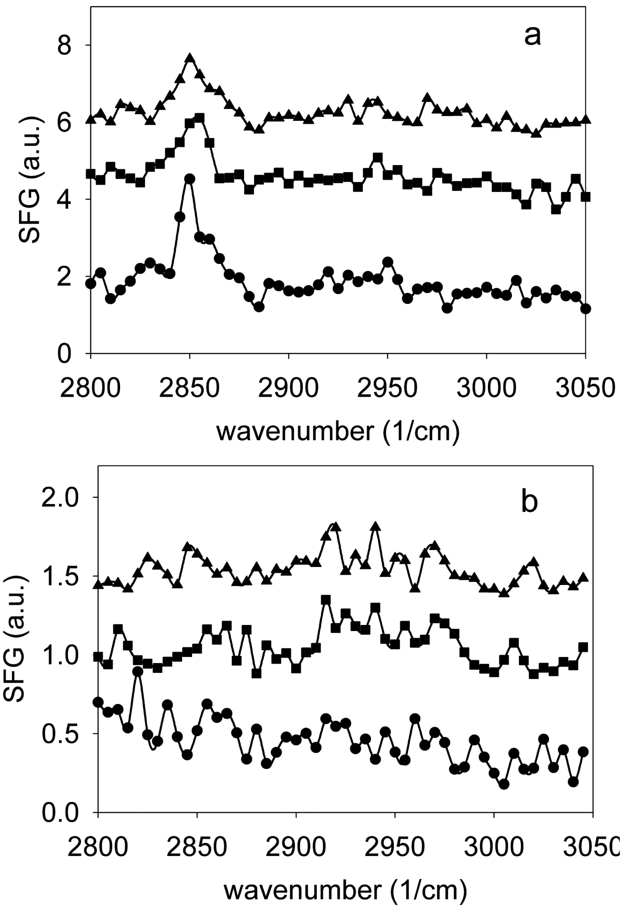

FIGURE 5. (a) SFG spectra of silicone in contact with TDFTMS at the initial contact (circles), 15 min after contact (squares), and 30 min after contact (triangles). (b) SFG spectra of silicone in contact with the TDFTMS/MVS mixture at the initial contact (circles), 15 min after contact (squares), and 30 min after contact (triangles). Spectra are offset.

and the silane signal would have decreased. Also of note, unlike the other silanes, there was no signal from the silicone elastomer at the interface between silicone and TDFTMS. This indicates that the silicone methyl groups lay down at this interface due to interactions with the fluorinated silane.

SFG spectra of silicone in contact with the TDFTMS/MVS mixture, also in Figure 5, showed no discernible signal from either TDFTMS or the silicone elastomer. The lack of a silicone elastomer signal indicates that the silicone methyl groups lay down at the interface, as they did at the interface with neat TDFTMS. The lack of a TDFTMS signal may have been due to a variety of factors. First, like OTMS, MVS may have acted to disorder TDFTMS at the silicone elastomer interface. This would cause the SFG signal to disappear. Also, like OTMS, MVS may have preferentially interacted with the silicone elastomer, causing it to cover the interface. However, because no signal that could be attributed to MVS was observed, this is less likely. A third explanation is that MVS facilitated the diffusion of TDFTMS into the silicone elastomer, which would further disorder the interface, causing a loss in the signal.

The interfaces between silicone and TDFTMS and between silicone and the TDFTMS/MVS mixture exhibited behavior different from those with γ-GPS and the γ-GPS/MVS mixture and with OTMS and the OTMS/MVS mixture. Unlike the other interfaces, the silicone methyl groups appeared to lay down when contacted to the fluorinated silane and its mixture with MVS. Further, the interface between silicone and TDFTMS showed evidence of either a slow interfacial silane reorientation or slow diffusion of silane into silicone. Like the OTMS/MVS mixture, there was no evidence of the TDFTMS methoxy groups ordering at the silicone interface when mixed with MVS. As discussed earlier, of the systems studied, only the γ-GPS/MVS mixture acts as an adhesion promoter. Because neither OTMS nor TDFTMS ordered at the silicone interface when mixed with MVS, this is further verification that the ability

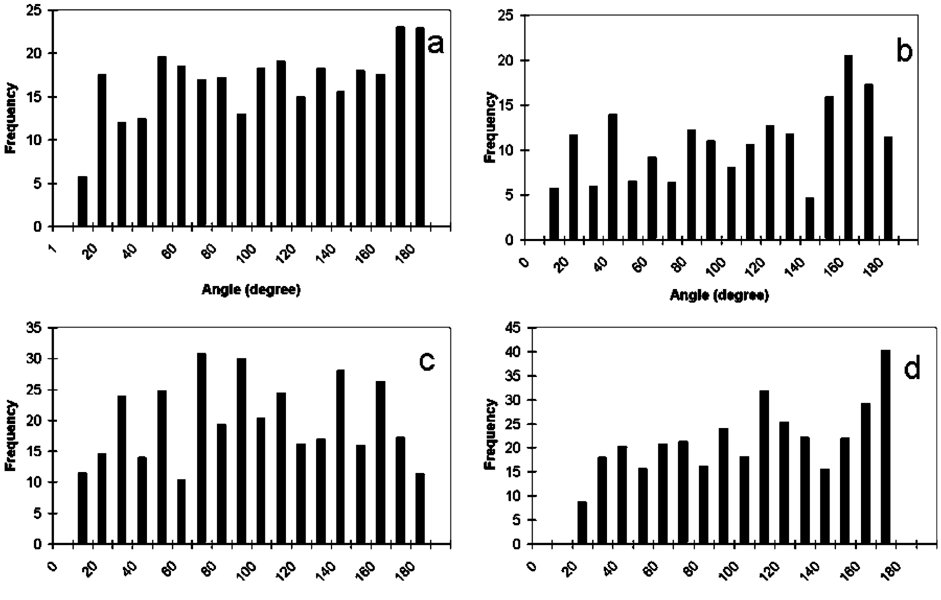

FIGURE 6. Silane methoxy angle distribution at the silicone interface as calculated from MD simulations for (a) γ-GPS, (b) γ-GPS in the γ-GPS/MVS mixture, (c) OTMS, and (d) TDFTMS.

of the γ-GPS methoxy groups to maintain order at the silicone interface when mixed with MVS may be a necessary prerequisite condition for the γ-GPS/MVS mixture to act as an adhesion promoter in polymer/silicone elastomer systems. Perhaps the silane adhesion-promoting mixture needs to be oriented in this way to participate in an adhesion mechanism, such as chemical bonding or the formation of an interpenetrating network. Such mechanisms are currently being investigated and will be reported in a future publication.

4. MD Simulation Studies of Silicone in Contact with Silanes and Silane Mixtures. Histograms of the calculated silane methoxy orientation distributions for γ-GPS, γ-GPS in the γ-GPS/MVS mixture, OTMS, and TDFTMS at the silicone interface, incorporating the correction for variation in a solid angle, are shown in Figure 6. As can be seen, the methoxy groups of all silanes exhibited broad, random orientation distributions in our simulations. This indicates that none of the silanes' methoxy groups exhibited strong, specific interactions with silicone that would lead to a narrow orientation distribution. The broad angle distributions calculated from the MD results confirmed inferences from the SFG spectra that the silane methoxy groups exhibited broad methoxy angle distributions at the silicone interface, although it did not account for the ordering of the silane methoxy groups inferred from SFG experiments. This may be due to the difference in time scales probed: 50 ps for the MD simulations versus 30 min in the case of our SFG experiments. That is, it is possible that ordering of the silane methoxy groups at the silicone interface simply occurred on a longer time scale than could be studied with MD simulations.

IV. CONCLUSIONS

The surface- and interface-sensitive nonlinear optical technique SFG was used to study the molecular structures of the interfaces between silicone elastomers and silanes, as well as their mixtures with MVS. The silane γ-GPS and the known adhesion-promoting mixture of γ-GPS and MVS were compared to two other silanes not used as adhesion promoters, OTMS and TDFTMS, and their mixtures with MVS. It was found that all neat silanes exhibited ordering of the methoxy groups at the silicone elastomer interface. However, only the γ-GPS methoxy groups remained ordered at the silicone interface when mixed with MVS. As previously discussed, MVS is necessary in an adhesion-promoting mixture because the MVS vinyl groups participate in the silicone cross-linking. Therefore, if a neat silane adopts a necessary orientation for adhesion at the silicone interface, it must also adopt that orientation when mixed with MVS to act as an effective adhesion promoter. Because only the known adhesion promoter maintained interfacial order when mixed with MVS, the ability of silane to order at the silicone interface in addition to its ability to order at the PET substrate interface may be a prerequisite condition for the mixture to promote adhesion at polymer/silicone elastomer interfaces. It is possible that the silane's interfacial conformation is necessary for it to participate in an adhesion mechanism, as is currently being studied. Further, MD simulations were used to confirm that the silane methoxy groups exhibited broad orientation angle distributions at the silicone elastomer interface.

Acknowledgment. This research is supported by the National Science Foundation (Grant CHE-044969) and Dow Corning Corporation. A.V.V. is supported by the Graduate Assistantships in Areas of National Need (GAANN).

REFERENCES AND NOTES

(1) Kinloch, A. J. *Adhesion and Adhesives Science and Technology*; Chapman and Hall: London, 1987.
(2) Mittal, K. L. *Adhesion Measurement of Thin Films, Thick Films and Bulk Coatings*; American Society for Testing and Materials: Philadelphia, PA, 1978.
(3) Yacobi, B. G.; Martin, S.; Davis, K.; Hudson, A.; Hubert, M. *J. Appl. Phys.* **2002**, *91*, 6227–6262.
(4) Charles, H. M. *Engineered Materials Handbook: Adhesives and Sealants*; ASM International: Materials Park, OH, 1990; Vol. 3.
(5) Feresenbet, E.; Raghavan, D.; Holmes, G. A. *J. Adhesion* **2003**, *79*, 643–665.
(6) Sathyanarayana, M. N.; Yaseen, M. *Prog. Org. Coat.* **1995**, *26*, 275–313.
(7) Suzuki, T.; Kasuya, A. *J. Adhesion Sci. Technol.* **1989**, *3*, 463—473.
(8) Walker, P. *Adhesion Promoters*, 1st ed.; Elsevier: London, 1987.
(9) Mine, K.; Nishio, M.; Sumimura, S. U.S. Patent 4,033,924, July 5, 1977.
(10) Schulz, J. B. U.S. Patent 4,087,585, May 2, 1978.
(11) Gray, T. E.; Lutz, M. A. U.S. Patent 5,595,836, Jan 21,1997.
(12) Bain, C. D. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1281–1296.
(13) Buck, M.; Himmelhaus, M. *J. Vac. Sci. Technol. A* **2001**, *19*, 2717–2736.
(14) Lambert, A. G.; Davies, P. B.; Neivandt, D. *J. Appl. Spectrosc. Rev.* **2005**, *40*, 103–145.
(15) Shen, Y. R. *Nature* **1989**, *337*, 519–525.
(16) Shen, Y. R. *The Principles of Nonlinear Optics*; Wiley: New York, 1984.
(17) Chen, C.; Loch, C. L.; Wang, J.; Chen, Z. *J. Phys. Chem. B* **2002**, *107*, 10440–10445.
(18) Loch, C. L.; Ahn, D.; Chen, Z. *J. Phys. Chem. B* **2006**, *110*, 914–918.
(19) Loch, C. L.; Ahn, D.; Chen, C.; Wang, J.; Chen, Z. *Langmuir* **2004**, *20*, 5467–5473.
(20) Chen, C.; Wang, J.; Loch, C. L.; Ahn, D.; Chen, Z. *J. Am. Chem. Soc.* **2004**, *126*, 1174–1179.
(21) Loch, C. L.; Ahn, D.; Vázquez, A. V.; Chen, Z. *J. Colloid Interface Sci.* **2007**, *308*, 170–175.
(22) Wang, J.; Woodcock, S. E.; Buck, S. M.; Chen, C.; Chen, Z. *J. Am. Chem. Soc.* **2001**, *308*, 9470–9471.
(23) Wang, J.; Chen, C.; Buck, S. M.; Chen, Z. *J. Phys. Chem. B* **2001**, *105*, 12118–12125.
(24) Loch, C. L.; Ahn, D.; Chen, C.; Chen, Z. *J. Adhesion* **2005**, *81*, 319–345.
(25) Chen, C.; Wang, J.; Chen, Z. *Langmuir* **2004**, *20*, 10186—10193.
(26) Chen, Z.; Shen, Y. R.; Somorjai, G. A. *Annu. Rev. Phys. Chem.* **2002**, *53*, 437–465.
(27) Gracias, D. H.; Chen, Z.; Shen, Y. R.; Somorjai, G. A. *Acc. Chem. Res.* **1999**, *32*, 930–940.
(28) Kweskin, S. J.; Komvopoulos, K.; Somorjai, G. A. *Langmuir* **2005**, *21*, 3647–3652.
(29) Ye, S.; Morita, S.; Li, G. F.; Noda, H.; Tanaka, M.; Uosaki, K.; Osawa, M. *Macromolecules* **2003**, *36*, 5694–5703.
(30) Yurdumakan, B.; Nanjndiah, K.; Dhinojwala, A. *J. Phys. Chem. C* **2007**, *111*, 960–965.
(31) Ye, H. K.; Gu, Z. Y.; Gracias, D. H. *Langmuir* **2006**, *22*, 1863—1868.

(32) Opdahl, A.; Phillips, R. A.; Somorjai, G. A. *J. Polym. Sci., Part B* **2004**, *42*, 421–432.
(33) Li, Q. F.; Hua, R.; Chea, I. J.; Chou, K. C. *J. Phys. Chem. B* **2008**, *112*, 694–697.
(34) Briggman, K. A.; Stephenson, J. C.; Wallace, W. E.; Richter, L. J. *J. Phys. Chem. B* **2001**, *105*, 2785–2791.
(35) Chen, Z. *Polym. Int.* **2006**, *56*, 577–587.
(36) Ye, S.; McClelland, A.; Majumdar, P.; Stafslien, S.; Daniels, J.; Chisholm, B.; Chen, Z. *Langmuir* **2008**, *24*, 9686–9694.
(37) Vázquez, A. V.; Shephard, N. E.; Steinecker, C. L.; Ahn, D.; Spanninga, S.; Chen, Z. *J. Colloid Interface Sci.* **2009**, *331*, 408–416.
(38) Yurdumakan, B.; Harp, G. P.; Tsige, M.; Dhinojwala, A. *Langmuir* **2005**, *21*, 10316–10319.
(39) Hwang, M. J.; Stockfisch, T. P.; Hagler, A. T. *J. Am. Chem. Soc.* **1994**, *116*, 2515–2525.
(40) Deng, M.; Tan, V. B. C.; Tay, T. E. *Polymer* **2004**, *45*, 6399–6407.
(41) Kornherr, A.; Hansal, S.; Hansal, W. E. G.; Besenhard, J. O.; Kronberger, H.; Nauer, G. E.; Zifferer, G. *J. Chem. Phys.* **2003**, *119*, 9719–9728.
(42) Lee, C. Y.; McCammon, J. A.; Rossky, P. J. *J. Chem. Phys.* **1984**, *80*, 4448–4455.
(43) Carrasco, F.; Pages, P.; Lacorte, T.; Briceno, K. *J. Appl. Polym. Sci.* **2005**, *98*, 1524–1535.

AM900612R