

Sum Frequency Generation Vibrational Spectroscopic Studies on a Silane Adhesion-Promoting Mixture at a Polymer Interface

Cheryl L. Loch,[†] Dongchan Ahn,[‡] and Zhan Chen^{*,†}

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

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Sum frequency generation (SFG) vibrational spectroscopy was used to probe the interface between poly-(ethylene terephthalate) with deuterated ethylene glycol subunits (*d*₄-PET) and a silane adhesion-promoting mixture (SAPM) comprised of (3-glycidyloxypropyl)trimethoxysilane (γ -GPS) and a methylvinylsiloxanol (MVS). Such a mixture has been found to improve the adhesion of an addition-curing silicone elastomer to a range of plastic and metal substrates. Our results demonstrated that at the interface between *d*₄-PET and a SAPM with a γ -GPS/MVS ratio of 1:1 (w/w), the silane molecules not only segregated to the interface but also the methoxy headgroups likely adopted a greater net orientational order along the surface normal than at the *d*₄-PET/ γ -GPS interface. The effects of varying the silane/siloxane ratio and using different siloxane oligomers on interfacial structures were also examined. This study provides unique molecular-level insights into the prerequisite conditions for adhesion of curable silicone adhesives.

1. Introduction

Adhesives that can bond to polymers are widely used in almost every area such as the automotive, aviation and aerospace, construction, electronics, industrial assembly and maintenance, paints and inks, and beauty and personal care industries.^{1–4} From aircrafts, to automobiles, to marine vessels, replacing rivets and bolts with adhesives greatly reduces weight and fuel consumption, thereby conserving energy, environmental resources, and cost. For the same reason, engineering plastics are used instead of metal. Hence, the ability of adhesives to robustly bond to plastics is imperative for the design of more cost-efficient products. Silicone elastomers are widely used for sealing and bonding in industrial applications; however, the addition of adhesion-promoting compounds is often necessary for them to bond to many adherends, such as plastics.⁵ Silane coupling agents are among the most commonly used adhesion promoters, especially for silicone elastomers. Many organosilane-based adhesion promoters have been developed to enhance adhesion to metals and inorganic substrates, and research shows alkoxy silane-based adhesion promoters can also be quite effective for imparting adhesion to some engineering thermoplastics.^{6–9} One such adhesion promoter is a mixture of an epoxy-functional silane, (3-glycidyloxypropyl)trimethoxysilane (γ -GPS), and a methylvinylsiloxanol (MVS), the chemical structures of which are illustrated in Figure 1. Separately, γ -GPS and MVS do not enhance adhesion when incorporated into an addition-cured silicone elastomer. However, when combined, this silane adhesion-promoting mixture (SAPM) enhances the adhesion of silicones to many surfaces, including plastics such as poly(ethylene terephthalate) (PET).^{7,8} Unfortunately, the molecular-level understanding of adhesion mechanisms at

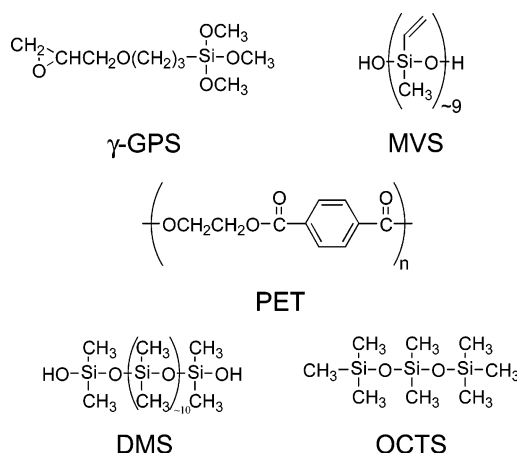


Figure 1. Chemical structures of the materials employed in this study.

silicone elastomer/polymer interfaces has not yet been fully developed. Such detailed understanding is needed for the systematic design of adhesives with the required performance for polymeric materials.

A significant limitation for most surface analytical methods used in adhesion studies is the inability to probe buried interfaces. As a surface/interface-sensitive nonlinear optical laser technique, sum frequency generation (SFG) vibrational spectroscopy has emerged as an invaluable tool to examine surfaces and interfaces,^{10–44} including buried polymer interfaces,^{29–44} in situ. SFG spectra concurrently reveal the coverage, net orientation, orientational order, and chemical environment of interfacial species, and because any surface or interface accessible by light can be probed by SFG, it is not only an ideal technique to elucidate the mechanisms that govern adhesion to plastics, but also has the potential to be developed into a nondestructive tool to evaluate adhesion at buried interfaces. Here we describe our SFG studies on the interfaces between PET and a SAPM. The interpretation of our SFG spectra will

* Author to whom all correspondence should be addressed. Fax: 734-647-4865.

E-mail: zhan@umich.edu.

[†] University of Michigan Department of Chemistry.

[‡] Dow Corning Corporation.

facilitate a better understanding of the interfacial structures of these molecules. In the future, we will use this insight to help elucidate the molecular structures of adhesion promoters, such as this SAPM, at addition-cured silicone elastomer/polymer interfaces and correlate these structures with adhesion.

2. Experimental Section

2.1. Materials. Deuterated polymers were employed in these SFG studies to avoid spectral confusion in the C–H stretching region. PET with deuterated ethylene glycol subunits (d_4 -PET, $M_v = 72\,000$) was obtained from Polymer Source, Inc. Dow Corning Corp. provided γ -GPS and MVS. All chemicals were used as received. Fused silica substrates (1-in. diameter, 1/8-in. thickness) were acquired from ESCO Products, Inc. Solid polymer films were prepared by spin-coating 1 wt % solutions of the polymer onto fused silica substrates using a spin-coater from Specialty Coating Systems. The films were placed under vacuum for at least 18 h prior to analysis to ensure adequate removal of the solvent.

2.2. SFG Experiment. The theory of SFG is well-developed and extensively covered in the literature.^{10–12} Details of our SFG setup and the experimental geometry employed to probe polymer/liquid interfaces are reported in previous publications.^{39–41} Briefly, the visible and infrared (IR) input beams travel through the fused silica substrate and overlap on the polymer surface or polymer/liquid interface temporally and spatially at incident angles of 60° and 54°, respectively, with the diameters of both beams at about 500 μm . The pulse energies of the visible and IR beams are ~ 200 and ~ 100 μJ , respectively. The frequency calibration of our SFG signal is always verified with a poly-(methyl methacrylate) reference prior to collecting SFG spectra. Previous research demonstrates that our SFG signals are dominated by the polymer/air or polymer/liquid interfaces with negligible contributions from the polymer/substrate interface or the polymer bulk.^{40–42} All SFG spectra shown were collected using the ssp (s-polarized sum frequency output, s-polarized visible input, and p-polarized IR input) polarization combination and were normalized by the intensities of the input IR and visible beams. This polarization combination of the input and output beams specifically probes those vibrational modes that have some component parallel to the surface normal (perpendicular to the interface).

3. Results and Discussion

The SAPM includes the alkoxysilane γ -GPS and a hydroxyl-terminated vinyl siloxane MVS. The d_4 -PET/ γ -GPS and d_4 -PET/MVS interfaces were characterized by SFG to determine which of the chemical groups of the contacting molecules adopted a net orientational order at those interfaces. The ssp SFG spectra acquired from the d_4 -PET surface in contact with MVS and γ -GPS are shown in Figure 2a. An SFG spectrum was also collected from the d_4 -PET/air interface (Figure 2a) to illustrate that only the peak attributed to the C–H stretching of the hydrogenated phenyl groups of the polymer (3075 cm^{-1}) was present in the spectrum.⁴⁵ A weak peak, centered at 2835 cm^{-1} , was the only spectral feature resolvable in the SFG spectrum from the d_4 -PET/ γ -GPS interface. This peak was characteristic of the symmetric C–H stretching of the silane methoxy headgroups.^{46–49} The SFG spectrum obtained from the d_4 -PET/MVS interface was dominated by two overlapping peaks centered at 2950 and 2970 cm^{-1} . These features must have originated from the C–H stretching of the vinyl and methyl groups of MVS. In the spectra depicted in Figure 2a, the spectral features and intensities did not change with time.

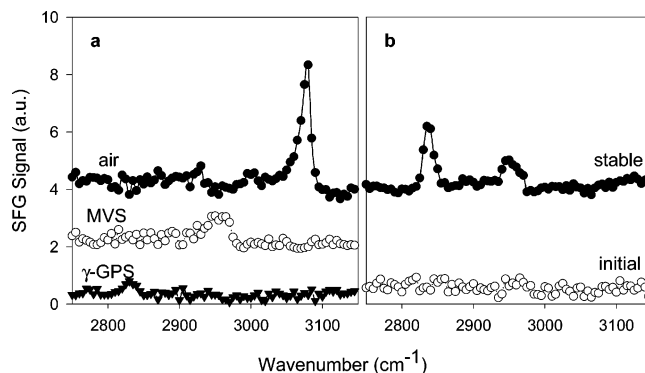


Figure 2. (a) SFG spectra collected from the interfaces between d_4 -PET and air, MVS, and γ -GPS. (b) SFG spectra collected from the d_4 -PET/1:1 SAPM interface immediately upon contact of the liquid with the polymer and once the spectral features and intensities stabilized.

The SFG spectra collected from the interface between d_4 -PET and a SAPM with a γ -GPS/MVS ratio of 1:1 (w/w) are illustrated in Figure 2b. The SFG spectrum obtained immediately after the polymer was placed into contact with the SAPM contained no resolvable peaks in the C–H stretching region. SFG spectra were continuously collected⁵⁰ after the initial spectrum; a peak at 2835 cm^{-1} appeared after about 10 min of contact, and its intensity remained stable thereafter. A smaller peak at 2950 cm^{-1} also emerged simultaneously. The peak at 2835 cm^{-1} was assigned to be the same as that collected from the d_4 -PET/ γ -GPS interface, although its final intensity was much greater in the SFG spectrum collected from the interface with the mixture. The feature at 2950 cm^{-1} may have had contributions from various C–H stretching modes from both γ -GPS and MVS.

The presence of the peak at 2835 cm^{-1} in the SFG spectrum collected from the d_4 -PET/ γ -GPS interface indicates that the silane methoxy headgroups have at least some interfacial net orientational order. The absence of this peak upon initial contact of d_4 -PET with the SAPM implies either that the γ -GPS molecules are not at the interface, or that they are present at the interface but the methoxy groups lack a net orientational order at the interface, or that they lie flat (parallel to the interface). The subsequent emergence of the peak at 2835 cm^{-1} with time suggests that not only do the silane molecules segregate to the d_4 -PET/SAPM interface but also that the methoxy groups have a net interfacial orientational order.

The increase in the SFG peak intensity upon going from the d_4 -PET/ γ -GPS interface to the d_4 -PET/SAPM interface could be the consequence of either a greater net orientational order of the silane methoxy headgroups or a change in their net orientation. It is well-known that more quantitative orientation information about interfacial functional groups can be deduced from SFG spectra collected using different polarization combinations of the input and output laser beams. The d_4 -PET/ γ -GPS and d_4 -PET/SAPM interfaces were examined by SFG using the ppp and sps polarization combinations; however, any SFG signals were at the noise level. This is similar to what was observed by Oh-E et al. at the C_1 polyimide interface.²⁹ In this study, SFG signals originating from the C–H stretching of the CH_3 groups of the interfacial molecules were only observed using the ssp polarization combination. It was concluded that the interfacial CH_3 groups had an average orientation along the surface normal with a broad orientation distribution. We believe that at both the d_4 -PET/ γ -GPS and d_4 -PET/SAPM interfaces the silane methoxy headgroups, on average, are oriented close to the surface normal with a possible broad distribution. Each

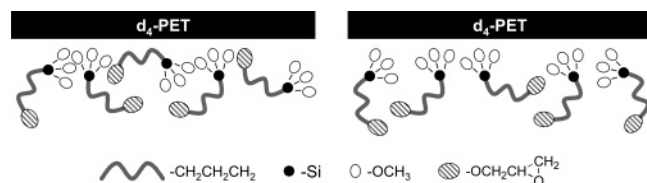


Figure 3. Schematic representations of the possible conformations of the silane molecules at the d_4 -PET/ γ -GPS (left) and d_4 -PET/SAPM (right) interfaces.

silane molecule consists of three methoxy groups, and thus even if the net orientation of the silane backbone, and hence the methoxy groups, is only slightly different at the two interfaces, the orientation distribution can be quite different. Therefore, the larger intensity of the peak from the silane methoxy headgroups at the d_4 -PET/SAPM interface implies that these groups have a relatively narrower orientation distribution and the γ -GPS molecules are more ordered toward the surface normal at this interface than at the d_4 -PET/silane interface (Figure 3). From this we can conclude that the presence of MVS in the SAPM must affect the behavior of the silane molecules at the interface with d_4 -PET. The segregation of the γ -GPS molecules to the polymer/SAPM interface may simply be due to their insolubility in MVS. The difference in the methoxy headgroup orientational order must be attributed to interactions between the γ -GPS and MVS molecules.

A number of mechanisms at different length scales may contribute to adhesion such as the segregation, ordering, and alignment of adhesion-promoting molecules at an interface, interfacial hydrogen or chemical bonding, and diffusion of molecules at the adhesive/adherend interface.^{2,51–54} For strongly adhering rigid polymer/elastomer interfaces, it is likely that some form of covalent bonding is operative, perhaps in concert with inter-diffusion of a particular species. It is unknown whether the absence of significant adhesion to certain polymers is due to simple unreactivity or to the lack of a prerequisite physical condition, such as the failure of the functional groups at the interface to establish the necessary concentration, order, or orientation for such reactions to occur. This current study reveals that upon mixing a silane with a siloxane, the silane methoxy headgroups adopt a greater net orientational order toward the surface normal at the interface with d_4 -PET in comparison to the d_4 -PET/silane interface without the addition of a siloxane. As disclosed by Schulz for metals, such a silane–siloxane mixture can enhance the adhesion of Pt-cured silicone elastomers far more effectively than the silane alone.⁸ We have corroborated these results with engineering thermoplastics such as 30% glass-filled poly(butylene terephthalate), a polyester homologous to PET, in heat-curing systems. Analysis of this substrate by XPS reveals that the filler is not present on the surface. For a Pt-cured adhesive, whose composition included 1.75% of the SAPM with a 1:1 silane/siloxane ratio and was cured for 1 h at 150 °C, adhesion tests using the single overlap test method resulted in failure of the PBT substrates, rather than the adhesive/PBT interface, indicating that the bond strength of the adhesive to PBT at the interface was in excess of 590 psi. We have qualitatively observed that a similar addition-cured silicone elastomer containing only γ -GPS cured onto a PET (or d_4 -PET) film is easily removed; however, one that contains the SAPM cannot be peeled off. More quantitative adhesion test results with PET will be presented in the future. Our SFG results here provide evidence supporting the hypothesis that interfacial ordering and orientation may be correlated to adhesion strength. We are currently incorporating the SAPM and other adhesion promoters into silicone adhesives and probing various polymer/

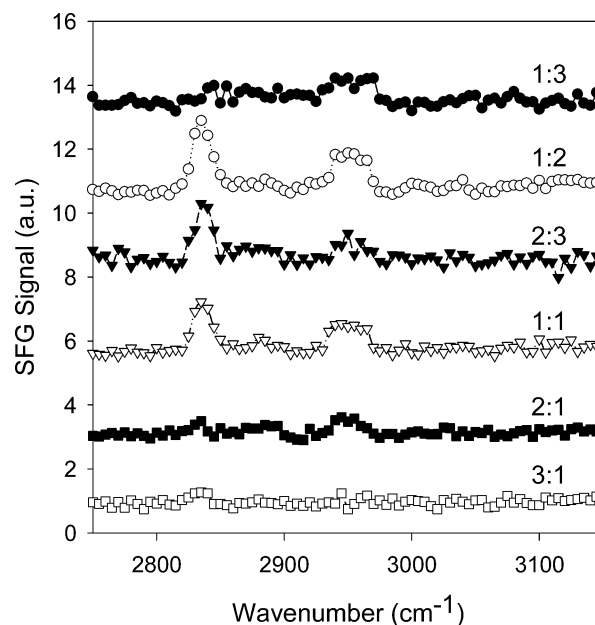


Figure 4. Stable SFG spectra collected from the d_4 -PET/SAPM interfaces with different γ -GPS/MVS ratios.

addition-cured silicone elastomer interfaces, in situ, using SFG. By examining such parameters as cure time, cure temperature, and adhesion promoter structure and concentration on both the interfacial structures, as deduced by SFG, and adhesion strength, a relationship between the two may be elucidated. The results of these studies will be reported in the future.

SFG spectra were also collected from the d_4 -PET/SAPM interfaces in which the γ -GPS/MVS ratio was varied from 3:1 to 1:3 (Figure 4). As was observed in the SFG spectra from the interface with the 1:1 SAPM, all of these spectra changed with time. The spectra presented in Figure 4 were obtained once the spectral features and intensities no longer varied. The SFG spectra from the d_4 -PET/SAPM interfaces in which the silane/siloxane ratios were 1:1, 2:3, and 1:2 were almost identical in that they were dominated by the silane methoxy peak at 2835 cm^{-1} with the spectral feature centered at 2950 cm^{-1} also present. However, once there was three times the amount of MVS as γ -GPS, these peaks were no longer completely resolvable in the SFG spectrum. Similarly, the intensity of the peak at 2835 cm^{-1} in the SFG spectra collected from interfaces with more γ -GPS than MVS in the SAPM was much smaller.

These SFG spectra suggest that even when the effective amount of silane in the SAPM is decreased in the bulk, the γ -GPS molecules still segregate to the d_4 -PET surface and the methoxy headgroups have a net orientational order toward the surface normal, similar to what was observed at the interface with equal amounts of silane and siloxane. However, there must be a minimum amount of γ -GPS in the SAPM mixture for a resolvable ssp SFG signal to be generated at the d_4 -PET/SAPM interface. Contrastingly, when there is more of the silane than the siloxane in the SAPM, the SFG spectra collected from these interfaces are much different than that from the interface with the 1:1 SAPM. The peak at 2835 cm^{-1} is almost unresolvable, indicating that the methoxy headgroups of γ -GPS do not have much orientational order (or lie flat) at the interface. Thus, there must be a minimum amount of MVS in the SAPM to induce the change in the net orientational order of the silane molecules. It is interesting to note that the silane/siloxane ratios that provided the greater peak intensities at the d_4 -PET/SAPM interfaces are similar in magnitude to the weight ratio range of 0.25–1.8 claimed to be effective for adhesion promotion in

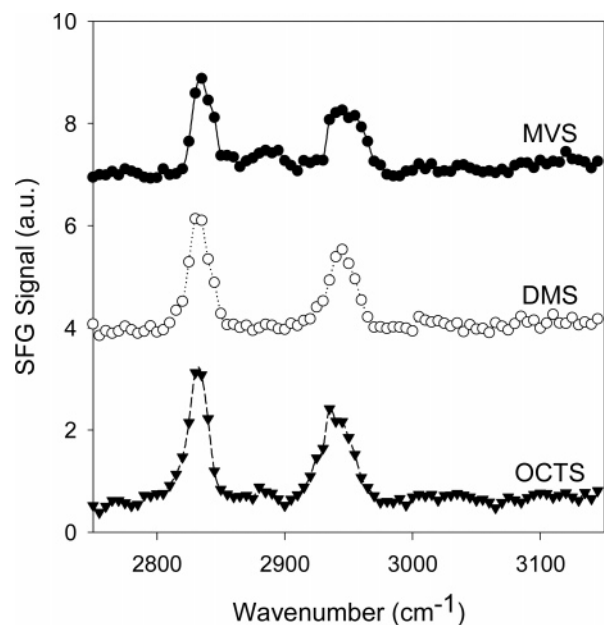


Figure 5. SFG spectra collected from the interfaces between d_4 -PET and 1:1 (silane/siloxane) mixtures of γ -GPS and different siloxanes.

silicone elastomers.^{7,8} This is evidence that interfacial structure, as deduced by SFG, can prove to be important in determining adhesive strength.

As illustrated in Figure 1, MVS features terminal hydroxyl and pendant vinyl groups, which provide structural contrast from the poly(dimethyl siloxane) (PDMS) that constitutes the bulk of a silicone elastomer matrix. To determine if the hydroxyl and vinyl groups of the MVS molecules interact with γ -GPS molecules to induce the increase in net orientational order toward the surface normal of the silane methoxy headgroups at the d_4 -PET/SAPM interface, dimethylsiloxanol (DMS) of similar chain length and a dimethylsiloxane oligomer, octamethyltrisiloxane (OCTS), were mixed with γ -GPS in a 1:1 ratio and placed into contact with the polymer. It is noted that DMS contains no vinyl groups in its structure, while OCTS lacks both vinyl and hydroxyl functionalities. The chemical structures of DMS and OCTS are also shown in Figure 1. SFG spectra were collected from the d_4 -PET/SAPM interfaces in which DMS or OCTS were substituted for MVS (Figure 5). The SFG spectrum from the d_4 -PET/SAPM with MVS is also shown in Figure 5 for reference. Again, the initial SFG spectra collected from these interfaces revealed no resolvable peaks; however, upon subsequent scans the peak at 2835 cm^{-1} emerged as the silane molecules must have segregated to the interfaces and the methoxy headgroups adopted a net orientation there. The SFG spectra obtained after the spectral features and intensities stabilized are presented in Figure 5. The three spectra are very similar to one another although the siloxane used in the SAPM is different for each spectrum collected. These results suggest that it is neither the vinyl nor the hydroxyl groups of MVS that induce the methoxy headgroups of the γ -GPS molecules in the SAPM to segregate to the interface with d_4 -PET and adopt a net orientational order. Indeed other oligomeric siloxanes such as DMS and OCTS appear to have the same effect. Increasing siloxane chain length will be tested soon.

It is speculated from these data that the enhancement in the adhesion of an addition-cured silicone elastomer to plastics provided by the SAPM comprised of γ -GPS and MVS may be due to both interfacial and bulk effects. For example, MVS induces the silane methoxy headgroups to adopt a greater net orientational order with respect to the polymer surface normal.

However, the vinyl groups must be present to react with the silicone matrix as it cures. As previously disclosed, to provide a more complete understanding of the mechanism of the adhesion promotion, we are currently studying silane ordering at the addition-cured silicone elastomer (with SAPM)/polymer interfaces, and such results will be reported in the future in conjunction with adhesion test data of these model silicone adhesives.

4. Conclusions

Using SFG we have demonstrated that at the buried d_4 -PET/SAPM interface, the γ -GPS molecules segregate to the interface and the methoxy headgroups adopt a net orientational order. It appears that when combined with a siloxane such as MVS, the silane methoxy headgroups exhibit an increase in their net interfacial orientational order toward the polymer surface normal when compared to the interface with the silane alone. This research provides insight into the important coordinating roles played by oligomeric siloxanes, at the molecular level, in adhesion to polymers.

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