Headgroup Effect on Silane Structures at Buried Polymer/Silane and Polymer/Polymer Interfaces and Their Relations to Adhesion

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Introduction

SFG is a second order nonlinear optical technique that is surface sensitive due to its selection rules.

Information

- on surface functional group identity,
- surface coverage,
- orientation distribution,
- ordering

can be deduced by analyzing polarized SFG spectra.

PDMS - poly(dimethyl siloxane)
PET - poly(ethylene terephthalate)
γ-GPS - (3-glycidoxypropyl) trimethoxysilane
γ-GPMS - (3-glycidoxypropyl) methyl-dimethoxysilane
γ-GPMS - (3-glycidoxypropyl) dimethyl-methoxysilane
MVS - Methylvinylsiloxanol

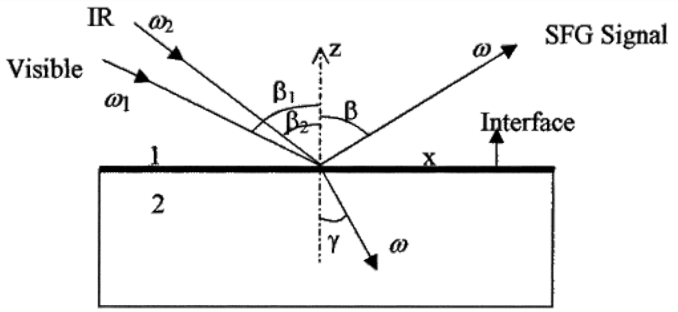
They probed interfaces between

- PET and γ-GPS (with three methoxy groups),
- PET and γ-GPMS, with two methoxy groups and one methyl group,
- PET and γ-GPDMS, with one methoxy group and two methyl groups,
- their mixtures with MVS,
- PET and uncured or cured silicone with different silanes and their mixtures with MVS.

SFG spectra detected at different interfaces were correlated to adhesion testing results.

Theoretical Background

Method To Fit SFG Spectra:



The SFG output intensity in the reflected direction:

$$I(\omega) = \frac{8\pi^3\omega^2 \sec^2\beta}{c^3 n_1(\omega_1) n_2(\omega_2)} \left|\chi^{(2)}_{eff}\right|^2 I_1(\omega_1) I_2(\omega_2) \ldots\ldots\ldots \text{(1)}$$

$$\chi^{(2)}_{eff,ssp} = L_{yy}(\omega)\, L_{yy}(\omega_1) L_{zz}(\omega_2) sin\beta_2 \chi_{yyz} \ldots\ldots\ldots (2)$$

With IR–visible SFG, if the IR frequency is near vibrational resonance, can be written as

$$\chi^{(2)}_{eff} = \chi_{nr} + \sum \frac{A_q}{\omega_2 - \omega_q + i\Gamma_q} \ldots\ldots\ldots (3)$$

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A_q, ω_q, and Γ_q can be obtained by fitting the SFG spectra.

$$\chi^{(2)}_{ijk} = N \sum_{l,m,n} \langle (\hat{\imath}\cdot\hat{l})(\hat{\jmath}\cdot\hat{m})(\hat{k}\cdot\hat{n})\rangle \beta_{lmn,q} \ldots\ldots\ldots (4)$$

The SFG hyperpolarizability tensor is a product of the IR transition dipole moment and the Raman polarizability tensor:

$$\beta_{lmn,q} \propto \frac{\partial \alpha^*_{lm}}{\partial Q_q} \frac{\partial \mu_n}{\partial Q_q} \ldots\ldots\ldots (5)$$

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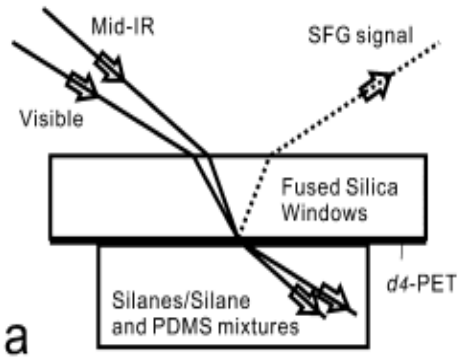
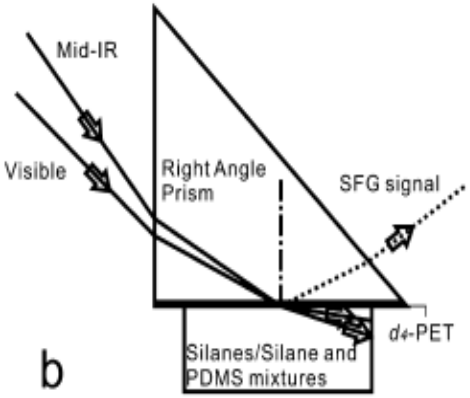
In summary, SFG has a superb surface sensitivity, which can probe molecular level structures of surfaces/interfaces *in situ* in real time.

NCA, Experiment





A window geometry (Fig.a)**:**

$$\chi_{eff}^{(2)} = L_{yy}(\omega)L_{yy}(\omega_1)L_{zz}(\omega_2)sin\beta_2\chi_{yyz}$$

$L_{ii}\,(i = x, y, z)$ are the Fresnel coefficients.

$$\left.\begin{aligned} L_{yy}(\omega) &= \frac{2n_1(\omega)cos\gamma}{n_1(\omega)cos\beta+n_2(\omega)cos\gamma} \\ L_{zz}(\omega) &= \frac{2n_2(\omega)cos\beta}{n_1(\omega)cos\gamma+n_2(\omega)cos\beta}\left(\frac{n_1(\omega)}{n'(\omega)}\right)^2 \end{aligned}\right\} \ldots\ldots(6)$$

$$n_1(\omega)sin\beta = n_2(\omega)sin\gamma$$

Paulo B. Miranda, PhD Thesis , 1998

A near critical angle (NCA) geometry: The incident angles of the visible was 57° and mid-IR input beams was 54° relative to the surface normal (Fig.b).

The calculated refractive angle of the signal at the interface, e.g., d_4-PET/silicone interface is ~81°.

<u>Larger refractive angle provides stronger reflection, which increases the SFG signal intensity detected.</u>

$$\cos\gamma \to 0, \gamma \to 90° \Rightarrow L_{yy}(\omega) = \frac{2n_1(\omega)cos\gamma}{n_1(\omega)cos\beta}, L_{zz}(\omega) = \frac{2n_2(\omega)cos\beta}{n_2(\omega)cos\beta}\left(\frac{n_1(\omega)}{n'(\omega)}\right)^2$$

$$\Rightarrow L_{yy}(\omega), L_{zz}(\omega) \nearrow \Rightarrow \chi_{eff}^{(2)} \nearrow \Rightarrow \text{from Eq (1) } [I_{SFG}(\omega) \propto \left|\chi_{eff}^{(2)}\right|^2 I_1(\omega_1)I_2(\omega_2)] \Rightarrow I_{SFG}(\omega) \nearrow$$

Materials

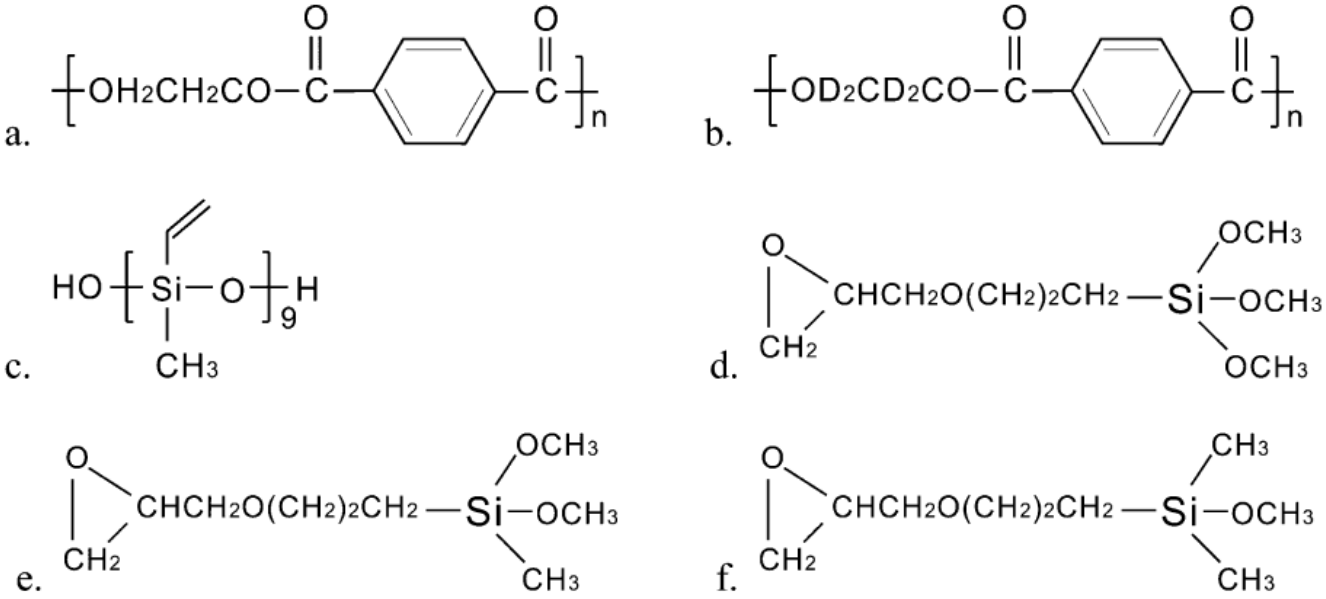


Figure 1. Chemical structures of polymers and silanes employed in the study:
(a) Poly(ethylene terephthalate) (PET);
(b) PET with aliphatic chain deuterated (d4-PET);
(c) Methylvinylsiloxanol (MVS);
(d) (3-glycidoxypropyl) trimethoxysilane (γ-GPS);
(e) (3-glycidoxypropyl) methyldimethoxysilane (γ-GPMS);
(f) (3-glycidoxypropyl) dimethyl-methoxysilane (γ-GPDMS).

These silanes share the same backbone and epoxy end group but have different headgroups.

Results And Discussion

d4-PET and MVS or Silicone (without Silanes)

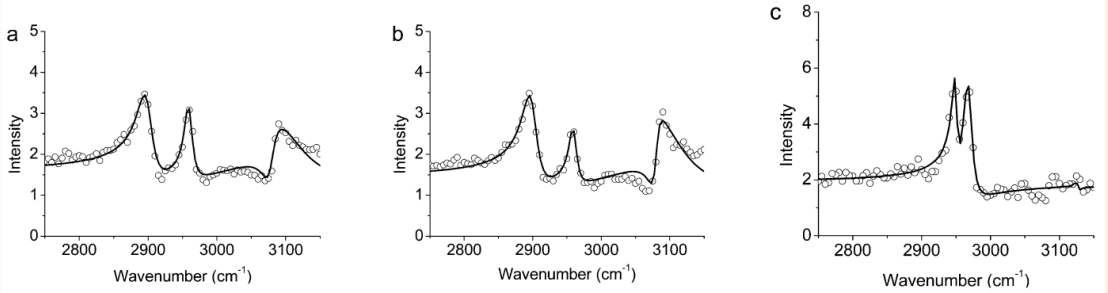


Figure 4. SFG spectra collected from (a) the d_4-PET/uncured silicone interface, (b) the d_4-PET/cured silicone interface, and (c) the d_4-PET/MVS interface. The dots are experimental data and the lines are fitted results.

d4-PET and Uncured Silicone Mixed with Silane or Silane–MVS Mixture

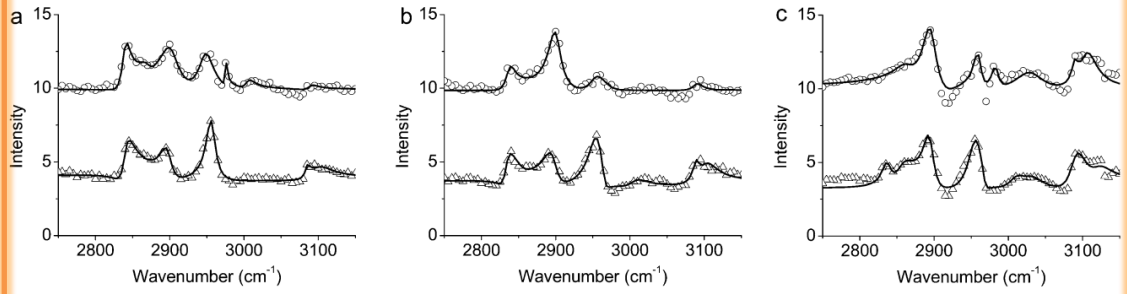


Figure 6. SFG spectra collected from the interfaces between d_4-PET and uncured silicones mixed with (a) γ-GPS (Δ) and γ-GPS:MVS (), (b) γ-GPMS (Δ) and γ-GPMS:MVS (), and (c) γ-GPDMS (Δ) and γ-GPDMS:MVS (). The dots are experimental data and the lines are fitted results.

d4-PET and Cured Silicone Mixed with Silane or Silane–MVS Mixture

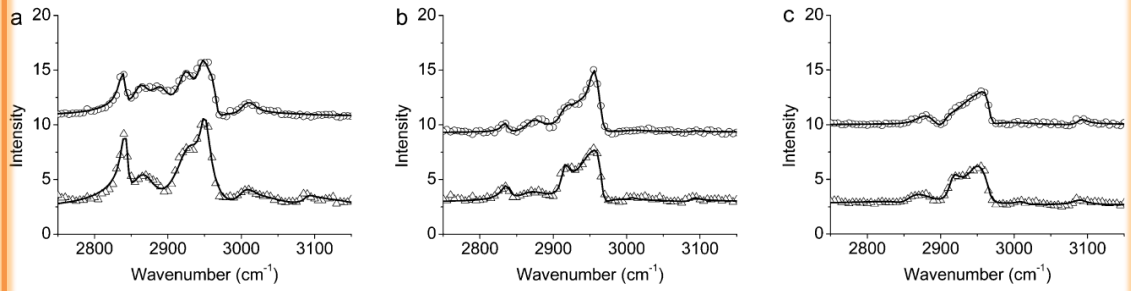


Figure 7. SFG spectra collected from the interfaces between d_4-PET and cured silicone with (a) γ-GPS (Δ) and γ-GPS:MVS (), (b) γ-GPMS (Δ) and γ-GPMS:MVS (), and (c) γ-GPDMS (Δ) and γ-GPDMS:MVS (). The dots are experimental data and the lines are fitted results.

d4-PET and Silane or Silane–MVS Mixture

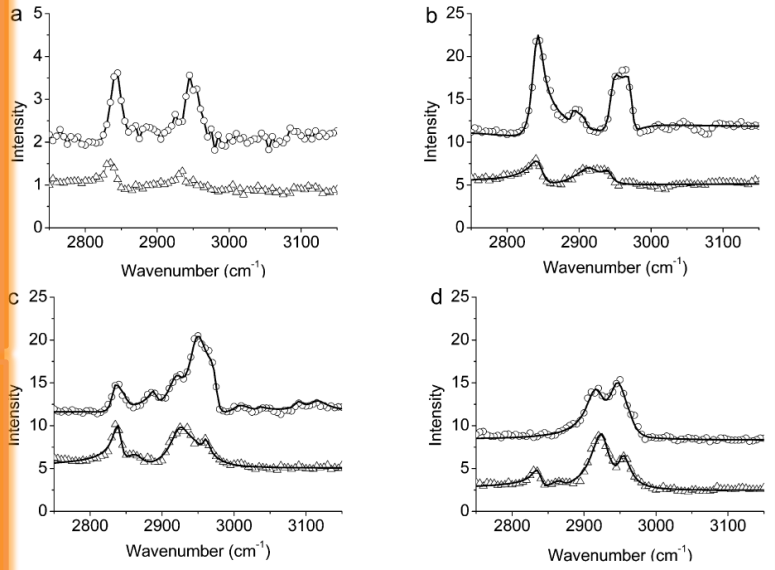
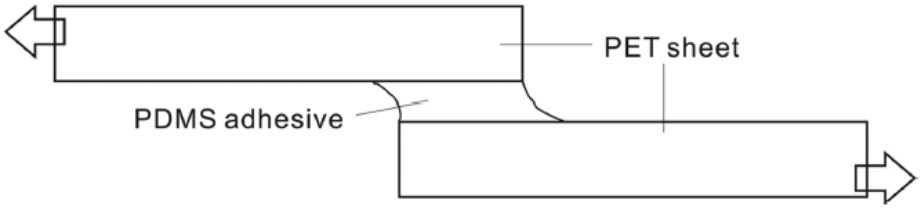


Figure 5. SFG spectra collected from (a) the d_4-PET/γ-GPS (Δ) and d_4-PET/γ-GPS:MVS interfaces () using the window geometry, (b) the d_4-PET/γ-GPS (Δ) and d_4-PET/γ-GPS:MVS interfaces () using the NCA geometry, (c) the d_4-PET/γ-GPMS (Δ) and d_4-PET/γ-GPMS:MVS interfaces () using the NCA geometry, (d) the d_4-PET/γ-GPDMS (Δ) and d_4-PET/γ-GPDMS:MVS interfaces () using the NCA geometry. For panels b–d, the dots are experimental data and the lines are fitted results.

Adhesion Testing

- The adhesion test on ASTM D3163 Standard with some modifications using an Instron 5544 mechanical test machine.
- PET sheet was cut into small pieces of the same size [30.0(width) × 12.0 (overlap length) mm^2] .
- The PDMS adhesive thickness is about 0.2 mm.
- The bonded PET pieces were pulled apart with a pulling speed of 1.3 mm/min.



- pure silicone only has weak adhesion to PET (<1 MPa).
- γ-GPDMS with/without MVS does not increase the adhesion between the adhesive and PET (<1 MPa).
- adding epoxy silanes γ-GPS and γ-GPMS to silicone increases the adhesion strength between silicone and PET (1–3 MPa).
- the γ-GPS:MVS mixture or the γ-GPMS:MVS mixture in silicone leads to much stronger adhesion to PET (3–5 MPa).

- the adhesion failure for all samples except PDMS γ-GPS:MVS mixture and PDMS γ-GPMS:MVS mixture happened at polymer/adhesive interfaces.

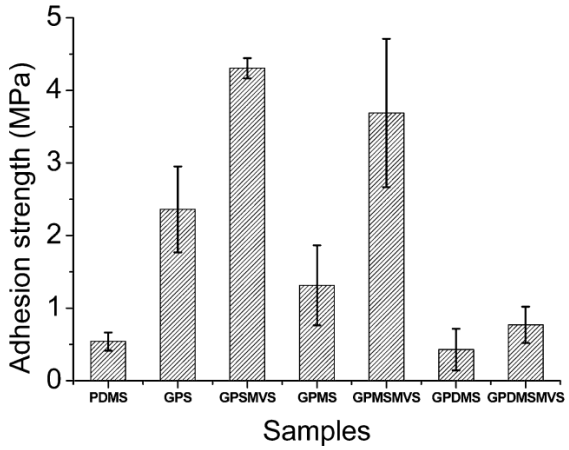


Figure 8. Adhesion shear test results. Strength = force/contact area.

Correlations between Adhesion Strength and Ordering of Interfacial Methoxy Groups

γ-GPS (three methoxy headgroups) > γ-GPMS (two methoxy headgroups) > γ-GPDMS (only one methoxy headgroup)

The more methoxy groups a silane has, the stronger the adhesion.
The mixing of MVS with silane greatly enhanced the adhesion between PET and PDMS silicone.

Adhesion testing results can be correlated to the SFG results quite well.

The SFG data indicated that at the PET/cured silicone interfaces:

- when γ-GPS (with/without MVS) and γ-GPMS (with/without MVS) were used -> interfacial segregation and ordering of methoxy headgroups could be observed {leading to strong adhesion}.
- when γ-GPDMS (with/without MVS) was used -> interfacial segregation and/or ordering of methoxy headgroups could not be detected {leading to weak adhesion}

The signal strength decreased substantially after the silicone was cured in the case of the two samples with the strongest adhesion (γ-GPS with MVS and γ-GPMS with MVS).

- They believe that the signal strength decrease is related to interfacial chemical reactions and/or diffusion processes that could lead to stronger adhesion.

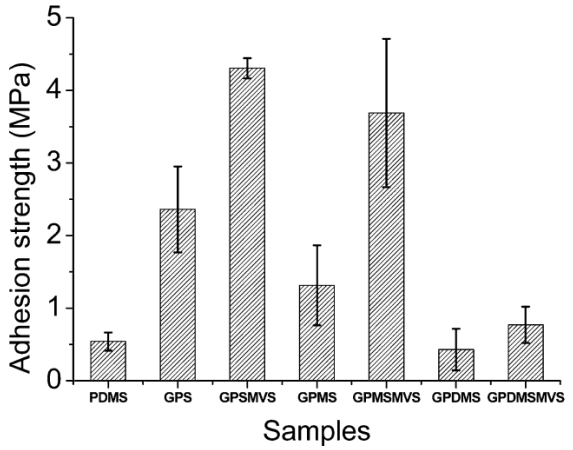


Figure 8. Adhesion shear test results. Strength = force/contact area.

Summary

- Silanes with different headgroups can behave differently at various interfaces.
- MVS greatly increased the methoxy group
  - ordering in γ-GPS at the interface,
  - slightly affected the interfacial methoxy ordering in γ-GPMS,
  - disordered the interfacial methoxy groups in γ-GPDMS.
- A range of methoxy group interfacial segregation and ordering behaviors was observed, which was correlated to measurements of adhesion strengths.
- Strong adhesion was detected at the PET/cured PDMS interfaces when γ-GPS (with or without MVS) and γ-GPMS (with or without MVS) were used, because of the interfacial segregation and ordering of methoxy headgroups before and after curing.
- The methoxy SFG signal strength decreased substantially after the silicone was cured when using silicone with either γ-GPS with MVS or γ-GPMS with MVS, and these two samples had the highest adhesive strength of those studied.
- Stronger adhesion is related to the interfacial segregation and ordering of methoxy groups at PET/uncured and cured silicone.
- This research also demonstrates that SFG is sensitive enough to detect the interfacial behavior of very small amount of silane molecules loaded into the polymer systems.