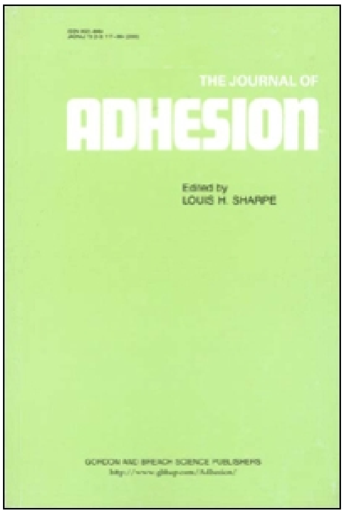

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Direct Probe of Interfacial Structure during Mechanical Contact between Two Polymer Films Using Infrared Visible Sum Frequency Generation Spectroscopy

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Direct Probe of Interfacial Structure during Mechanical Contact between Two Polymer Films Using Infrared Visible Sum Frequency Generation Spectroscopy

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Infrared-visible sum frequency generation spectroscopy (SFG) has been used to study the interface between poly(vinyl-N-octadecylcarbamate-co-vinyl acetate) (PVNODC) and polystyrene (PS) films during mechanical contact. The films were contacted using a deformable semispherical poly(dimethylsiloxane) (PDMS) lens that can be easily adapted to incorporate friction and adhesion force measurements. A strong methyl symmetric peak and Fermi resonance band associated with the alkyl side chains of PVNODC are observed in the SFG spectrum. This suggests that the interface structure during mechanical contact is more ordered than the structure observed for PS/PVNODC bilayer films annealed above the melting and glass transition temperatures of PVNODC and PS. Complementary contact mechanics measurements reveal a small adhesion hysteresis supporting our hypothesis that the interface structure during mechanical contact is not significantly different from the structure of the air interfaces before contact.

Keywords: Polymer adhesion; Polymer surface; Polymer interface; Alkyl side chain polymer; Surface restructuring; Surface transition; Nonlinear optics; Sum frequency generation

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INTRODUCTION

Mechanical contact between two soft solids, particularly polymers, is of fundamental importance in the areas of friction, adhesion, and contact mechanics [1–3]. Although there have been numerous studies on measurements of adhesion and friction using macroscopic (surface force apparatus [4] and mechanical tribometers [5]) and microscopic contact areas [6], there have been no direct measurements of interfacial structure during mechanical contact between two polymer surfaces. In order to understand adhesion hysteresis, friction, and mechanisms of energy dissipation at interfaces, it is important to study the structure of polymer surfaces upon mechanical contact. Some notable advances have been made in probing molecular level interface structure during macroscopic [7–10] and microscopic contacts of hard surfaces [11].

Here, we report the first direct measurement of the interfacial structure of two immiscible polymers brought in mechanical contact with each other. We based this study upon two developments: First, the demonstrated sensitivity of infrared visible sum frequency generation spectroscopy in a total internal reflection geometry (TIR-SFG) as a probe of hidden polymer–polymer interfaces [12–14]. SFG signals are enhanced by several orders of magnitude when the incidence angle of input beams is close to a critical angle for internal reflection, as given by Snell's law, providing the selectivity to study the interface after contact. Second, inspired by the PDMS lens innovations developed by Chaudhury and others [1, 15–17], we used the geometry of a soft elastomeric semispherical lens and a flat substrate provided by the prism face to generate a uniform and smooth contact area for use in conjunction with TIR-SFG. The contact mechanics theory for soft solids in this geometry was developed by Johnson, Kendall, and Roberts (JKR) [18]. The size of this contact area can be easily controlled by varying the normal force and radius of curvature. Moreover, by depositing films of different polymers on the elastomeric lens, this geometry can be used to study the interface between many different polymers and can be easily adapted to incorporate in situ friction and adhesion force measurements [19].

As a demonstration, we have studied the mechanical contact between an amorphous glassy polystyrene (PS) and alkyl side-chain polymer poly(vinyl-n-octadecyl carbamate-co-vinyl acetate) (PVNODC). This complements the measurements published on annealed bilayer interface between PS and PVNODC prepared using spin coating [12, 13]. The annealed PS/PVNODC interfacial structure is very different from that of the PS/air and PVNODC/air interfaces, indicating significant restructuring at the interface. But it is not clear whether this rearrangement takes place upon contact or after annealing the system above the T_m of PVNODC and T_g of PS. This is important to understand because adhesion hysteresis is often attributed to interfacial rearrangement on contact.

EXPERIMENTAL BACKGROUND

The sapphire prism and composite PDMS lens geometry used for these experiments is shown schematically in Figure 1. A polystyrene thin film (300 nm thick) was spin coated on a sapphire prism using a 5 wt% solution in toluene. The film was annealed under vacuum for three hours at 120°C. The elastomeric lenses for SFG measurements (3.6 mm radius-of-curvature) were prepared by placing drops of poly dimethyl siloxane (PDMS) resin (Dow Corning, Sylgard 184) in a polystyrene petri plate filled with distilled water. Small lenses (1 mm radius-of-curvature) for JKR measurements were made by placing small drops of PDMS on a glass slide (made hydrophobic by treatment with fluorosilane). The drops were cured as per manufacturer's recommendations and the unreacted resin was extracted by swelling in toluene.

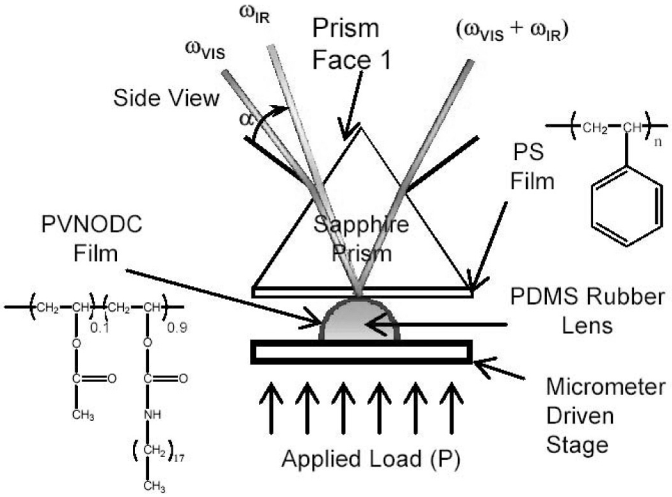

FIGURE 1 Schematic of the experimental geometry used to probe the mechanically formed contact interface between two polymer surfaces using TIR-SFG. One polymer film is coated on the sapphire surface and the other on top of a deformable elastomeric lens.

The second polymer film of a comb-like polymer, poly(vinyl-n-octadecyl carbamate-co-vinyl acetate) (PVNODC), was spin coated from 5 wt% solution in toluene on to a freshly cleaved mica surface. The PVNODC film was annealed under vacuum for three hours at 80°C. Following the method of Li et al. the PVNODC film was then floated off the mica surface in distilled water and placed on the surface of a cross-linked PDMS lens (pretreated for 5 s with oxygen plasma to improve adhesion between the PVNODC film and the PDMS lens), and dried under vacuum [20]. For the annealed bilayer film, a PVNODC film was floated off in water and was placed on top of a PS film on a sapphire prism substrate prepared as stated above, dried under vacuum, and then annealed again for 3 hours at 120°C.

The elastomeric composite lens was brought in mechanical contact with the polystyrene substrate using a micrometer stage. The SFG generating beam footprint is smaller than the size of the contact region. The SFG measurements were done at comparable contact pressures (0.1–0.3 MPa across the contact radius of 1 mm) to the JKR experiments (0.1–0.15 MPa across the contact radius of 0.13 mm). The details of the SFG spectrometer and the experimental geometry have been discussed in previous publications [12]. However, for the SFG spectra shown here the emitted SFG light was taken through a spectrometer increasing the effective resolution to $<5\,\mathrm{cm}^{-1}$.

RESULTS AND DISCUSSION

Figure 2 shows SFG spectra in the SSP polarization combination (S-polarized SFG beam, S-polarized visible beam, P-polarized IR beam) before and during mechanical contact between PVNODC and PS. The measurements upon contact were done at an incidence angle of 8 degrees (with respect to the prism face 1) and the total internal reflection condition is met only when the composite lens is in contact with the PS film (as illustrated by the weak SFG signals before contact with the lens). In addition, Figure 2 shows an SFG spectrum from the polymer–polymer interface of an annealed PS/PVNODC bilayer film taken using the same laser system. The results for annealed bilayers are comparable to those acquired previously using a different laser setup and are discussed elsewhere [13].

The peaks below $3000\,\mathrm{cm}^{-1}$ correspond to side chains of PVNODC and above $3000\,\mathrm{cm}^{-1}$ to the C–H stretching vibrations of the PS phenyl group. SFG spectra for PS/air and PVNODC/air have been published before [13, 21–23]. Vibrational assignments and discussion of functional group orientation have also been discussed previously for these interfaces [13, 21–23]. In brief, the main peak in the SSP

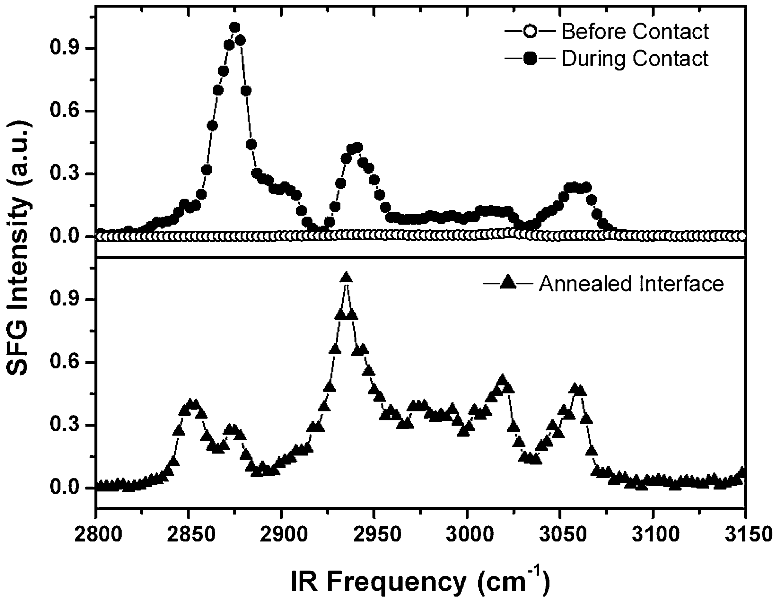

FIGURE 2 (Top Panel) SFG spectra in SSP polarization for PS/PVNODC interface before (○) and during mechanical contact (●). (Bottom Panel) SFG spectrum in SSP polarization for an annealed PVNODC/PS bilayer film. The intensities have been normalized to 1 for presentation.

spectrum for PS/air interface is at 3068 cm^{-1} corresponding to the ν_2 symmetric phenyl vibration of phenyl groups. The presence of only symmetric peaks indicates that the phenyl groups are oriented normal to the surface [21]. The two main peaks in the PVNODC/Air interface SSP spectrum are the methyl symmetric stretch (~2873 cm^{-1}) and Fermi resonance (~2931 cm^{-1}) [23]. This indicates that the surface is methyl terminated with well-ordered long alkyl side-chains in predominantly all-trans conformations [22, 23]. The annealed PS/PVNODC PVNODC interface spectrum also includes a methylene symmetric peak at 2844 cm^{-1}, a methylene asymmetric peak at 2920 cm^{-1}, a methyl asymmetric peak at ~2960 cm^{-1}, and a ν_{20b} asymmetric phenyl peak ~3024 cm^{-1} [13].

The four main peaks observed in the contact interface spectrum (Figure 2 top panel) are assigned to methyl symmetric, methyl Fermi, and two phenyl vibrational modes, ν_2 and ν_{20b}. The spectrum of the interface during mechanical contact between PS and PVNODC is different from the annealed PS/PVNODC bilayer interface (Figure 2 bottom panel). However, in general, the contact interface spectrum is similar to the spectra of PS/air and PVNODC/air interfaces observed before contact with a decrease in intensity of the phenyl peaks. The methyl peaks from PVNODC side chains do not change significantly upon contact; this indicates that the crystalline order found at the PVNODC/air interface is not perturbed during contact. Comparison of the spectra taken for PS/air interfaces before and after contact shows that the intensity of phenyl peak is lower after contact. These changes upon contact are minor in comparison to those observed after annealing and demonstrate that complete restructuring of the interface requires annealing above the transition temperatures of PVNODC and PS.

The JKR theory of contact mechanics indicates that a radial pressure or stress distribution will exist for contact between a sphere and a flat [18]. To probe the effect of this distribution, we have acquired SFG spectra at different positions in the contact spot and measured the SFG intensity as a function of position along the radius in the contact region. Currently, the resolution for this measurement is limited by the SFG generating footprint or the size of the spot where the lasers overlap to generate SFG. Figure 3 summarizes these results and provides a schematic of the contact spot to illustrate the measurement. The graph on the lower left side of Figure 3 shows the SFG intensity as a function of position along the contact spot (right ordinate) and the expected pressure or stress distribution based on the JKR theory (left ordinate). The SFG profile of the contact spot extends beyond the actual contact diameter and reflects the convolution of the actual contact spot size with the size of the SFG generating beam footprint.

The top and middle right of Figure 3 shows SSP polarization SFG spectra, labeled A and B acquired at the two different SFG footprint positions, as indicated by the shaded ellipses. These two foot print locations probe regions of the contact spot experiencing the corresponding shaded portions of the pressure distribution such that the average pressure in region A is approximately twice that in region B. The overlaid SFG spectra in the bottom right corner of Figure 3 show these same two spectra after normalization for the fraction of the contact area the SFG generating footprint covers. Clearly, this overlay indicates the difference in spectral features is negligible and that compression is not important to any spectral differences observed on contact.

To correlate the structure on contact with adhesion, we have performed JKR type contact mechanics measurements using an apparatus similar to that described by Mangipudi et al. [17]. On loading (Figure 4), we measure the work of adhesion $W_{\mathrm{loading}} = 46 \pm 3\,\mathrm{mJ/m^2}$. This value of W is expected for contact between methyl groups and PS

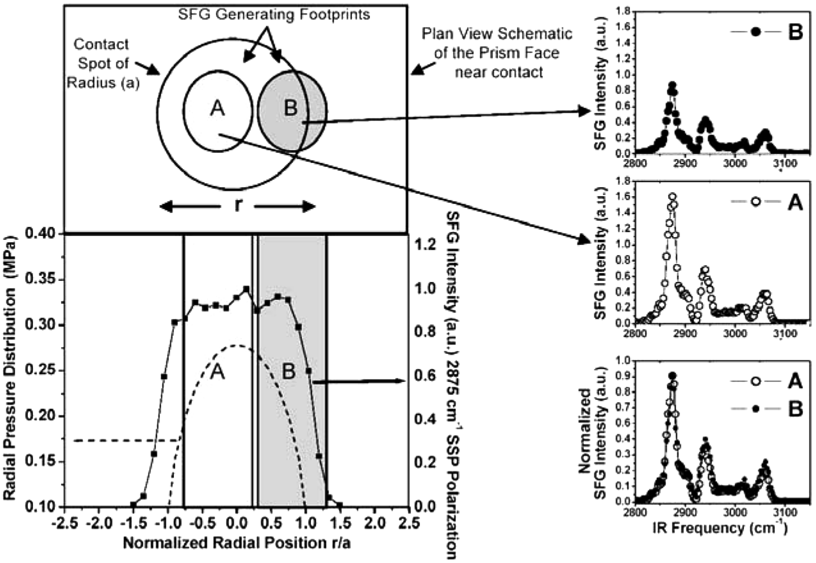

FIGURE 3 Plan view schematic of prism face near the contact spot (top left), plot showing SFG intensity and expected normal stress distribution across the diameter of the contact spot (bottom left). The ellipses overlaying the contact spot labeled A and B represent the SFG generating beam footprint positions at which the corresponding spectra on the right were taken (top and middle right). SFG spectra from positions A and B, normalized to correct for the area the SFG footprint at position B, which does not overlap the contact spot (bottom right). Both spectra are in the SSP polarization for $\phi_{\mathrm{IR}} = 8^{\circ}$.

[17]. On unloading, using the loading value of the elastic constant, K, we obtain a value of $\mathrm{W}_{\mathrm{unloading}} = 50 \pm 3\,\mathrm{mJ/m^2}$. The small adhesion hysteresis, clear in the difference between the loading and unloading W's, is due to restructuring of PS upon contact. The interfacial energy calculated from W and surface energies of PS [17] and PVNODC [20] assuming no rearrangement is $\sim 10\,\mathrm{mJ/m^2}$. The magnitude of $(\mathrm{W}_{\mathrm{loading}} - \mathrm{W}_{\mathrm{unloading}}) \approx 4\,\mathrm{mJ/m^2}$ is in qualitative agreement with the changes in orientation of the PS phenyl groups upon contact.

SUMMARY

In summary, we have demonstrated the first combination of SFG spectroscopy and JKR geometry as a means to study changes in interfacial molecular structure during mechanical contact. This study found that the structure during contact is similar to that of PS/air

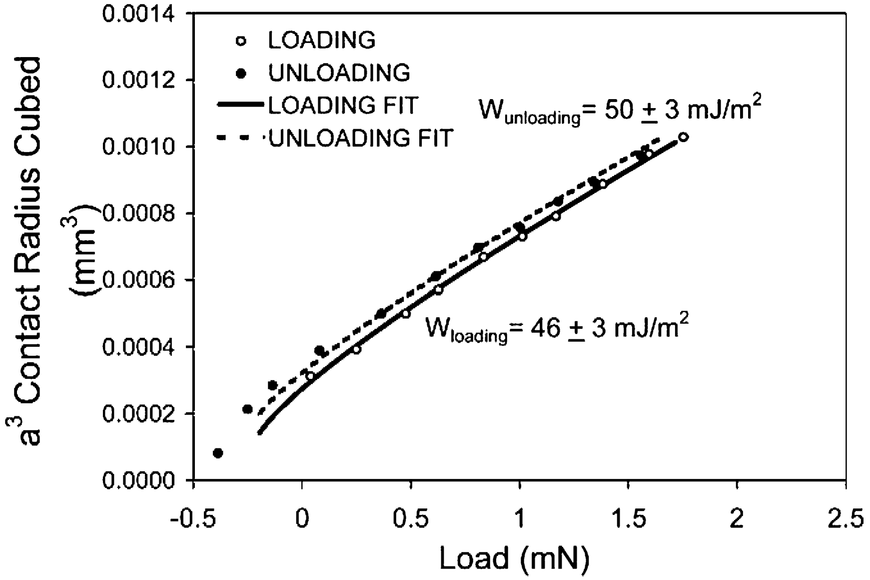

FIGURE 4 JKR Plot of the contact radius cubed, a^3, versus applied load, P, for contact between a PVNODC composite lens and a PS flat. Open symbols and closed symbols represent measurements during loading and unloading cycles, respectively.

and PVNODC/air before contact. This finding is in contrast to the more significant spectral and structural changes previously observed at the PS/PVNODC interface after annealing above the melting temperature of PVNODC. Experiments to probe the kinetics of interfacial restructuring upon heating and contact interfaces of non-crystalline polymers are the subject of our current and future work.

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