RESULTS AND DISCUSSION

The work of adhesion of the PS-DMS film can be theoretically derived and correlated to the spectroscopic results by finding the relationship between the PS-DMS film and the PS-DMS interface. The constant contrast of the bonds involved in adhesion changes, vibrational frequencies of these bonds will also change. If this is the case, the relationship between the work of adhesion of the PS-DMS film and its vibrational adsorption changes is important, which suggests a possible interaction between the work of adhesion and vibrational energy changes.

Special Measurements

From Table 1, we have a phenolospon cell adapted for spectroscopic measurements. The sample compartment utilizes a stationary clamping block to anchor the sample and a movable clamping block which is straddled to the load screw. The lead screw and clamping block elongate the sample while holding it in a position for infrared data acquisition. The screw, with 40 threads per inch, provides elongation of 0.635 mm per revolution, which converts to 0.00013 mm per revolution of 360. The cell design is such that the sample is sealed during data collection by clamping it between the cell top and bottom. The cell top, which allows the light to pass through the sample, contains a 50 cm window. The cell top, clamping blocks, and lead screw are attached by cap screws to the main cell frame and block. The cell block contains both tapped into it, which allows helium purge and cell pressure removal, and provides a path for the polarizing waves to reach the microphotometer detector.

The cell design is universal, allowing measurements of various samples such as films, aerogel, and fibers. The procedure of placing the sample, immersion by cell immersion, consists in removing the cell top, clamping the sample in the clamping blocks, turning the lead screw the desired amount to elongate the sample, purging the cell with helium for several minutes, pressurizing and collecting 450 scans at a 4 cm⁻¹ resolution on a Bruker FTS-180 FTIR spectrometer. The resolution frequency of the spectrometer is 5 kHz. The co-added sample scans were ratioed to a carbon black reference and transformed in into a computer for analysis utilizing Spectra Cube software.

The PA FTIR spectra of samples collected at 0.03 absorbance increments. All measurements were carried out in triplicate to verify reproducibility. Prior to the experiments on the double layer samples, PA-FTIR measurements were conducted on polyethylene substrate and the DMS diol assembly was used as references for the entire study.
The interaction in which two molecules with permanent dipole moments interact with each other can be expressed as

$$V_{dipole-dipole} = \frac{q_1 q_2}{r_{12}}$$

(7)

where $q_1$ and $q_2$ are the bond dipole moments, and $r_{12}$ is the orientation factor.

The component of the interaction force along a bond length $r$ when the substrate bond is at its equilibrium distance, can be described by the first derivative of the potential energy function $V(r)$ as shown by

$$F = -\frac{dV}{dr}$$

(8)

where $F$ and $V$ are empirically derived constants.

The component of the interaction force along a bond length $r$, when the substrate bond is at its equilibrium distance, can be described by the first derivative of the potential energy function $V(r)$ as shown by

$$\frac{dV}{dr} = \frac{q_1 q_2}{r_{12}^3}$$

(9)

The overall force of interactions is a sum of dipole and repulsive forces which can also be represented as the derivative of each potential energy term with respect to $r$.

$$F = F_{dip} + F_{rep} = -\frac{1}{\epsilon_0} \frac{q_1 q_2}{r_{12}^3} + \frac{1}{\epsilon_0} \left( V_{dip} - V_{rep} \right)$$

(10)

As a result of perturbation, vibrational frequency will change as well as the bond distance, and the force constants. To account for this, one can adopt an approach similar to solute-solvent interactions, and assume that the substitution frequency shift produced by the attractive and repulsive forces of the surrounding medium are proportional to the changes in bond length, $\Delta V^{1,13}$

$$\Delta v / v_0 = -\alpha \left( \Delta r / r_0 \right)$$

(11)

The equilibrium distance, $r_0$, is regarded as a distance at which the potential energy well reaches a minimum. As the bond is displaced from equilibrium, the potential energy well can be estimated by combining the equilibrium intermolecular potential, $V_{11}$ (Eqn. 1), and the interaction vibrational potential, $V_{12}$ (Eqn. 2).

The proportionality constant, $\alpha$, in Eqn. 11 depends on the properties of two interacting molecules. The $\alpha$ term can be determined by utilizing Lippert's rule$^{10}$, whereas the $\Delta V$ term can be evaluated using empirical correlation from Ondrej$^{11}$ and Hershfield$^{12}$ giving

$$\alpha = \frac{1}{\epsilon_0} \frac{1}{2} \frac{\hbar^2}{\epsilon_0} (\epsilon - 1)$$

(12)

From the above relationships, $\Delta W$ will be determined by integrating the force of interaction, $F$, over the limits of equilibrium bond distance in $v_0$, giving the work of adhesion:

$$\Delta W = \int F \, dr = \int F_{dip} + F_{rep} \, dr = \int \left( -\frac{1}{\epsilon_0} \frac{q_1 q_2}{r_{12}^3} + \frac{1}{\epsilon_0} \left( V_{dip} - V_{rep} \right) \right) \, dr$$

(13)

Using the experimental data and the above relationships, the work of adhesion can be calculated, and the correlation between spectroscopic measurements and microscopic properties of the interfacial region in a bilayer adhesion system can be made.

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REFERENCES


Figure 1. Schematic diagram of photoacoustic FT-IR cell adapted for rheo-photoacoustic measurement: A - microchannel compartment; B - indium for sample clamping; C, D - removable and stationary clamping blisters; E - sealed sample area; F - gas inlet for purging the cell.

Figure 2. Frequency shift plotted as a function of elongation for various coating thicknesses: A - 120 um, B - 150 um, C - 250 um, D - 250 um, E - 300 um, F - 340 um.

Figure 3. Frequency shift plotted as a function of coating thickness for various elongations: A - 1.7%, B - 1.8%, C - 6.0%, D - 3.9%, E - 10.8%.