Microwave Plasma Reactions on Polymer Surfaces and Molecular Level Adhesion
ATR and Step-Scan Photoacoustic FT-IR Spectroscopic Approaches

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Introduction:

Molecular level interactions that occur near surfaces and interfaces of organic coatings play a key role in adhesion and other interfacial processes. Although the magnitude of these interactions may vary, it is apparent that the strength and reversibility of interfacial reactions may induce stratification processes and therefore interfacial properties. For that reason, it is important to understand not only the origin of molecular level processes that govern physico-chemical processes near interfaces, but also molecular dynamics. In the context of interfacial chemistry, it is also important to be able to quantify molecular entities near interfaces because the presence of local non-homogeneity may have significant effects on adhesion. If a local concentration of one of the components is excessively high, the properties of this portion of the film will be altered. If one envisions this phenomenon in a context of the film-air (F-A) or film-substrate (F-S) interfaces which exhibit excess of surface/interfacial energy, an excessive migration to the F-A or F-S interfaces in order to compensate for the excess of energy will occur. With this background in mind let us focus on the molecular probes that can provide qualitative and quantitative information about interfacial processes, in particular, surface/interfacial reactions on polymers to promote surface adhesion, enhancement of biocompatibility, or the work of adhesion.

Attenuated Total Reflectance FT-IR Spectroscopy

The principles of ATR FT-IR spectroscopy are known, and one of the main advantages of ATR is the possibility of conducting depth penetration experiments. The penetration depth, \( d_p \), is expressed by the following equation:

\[
d_p = \frac{\lambda}{2\pi n_{c}^2 \sin^2 \theta - n^2}^{1/2}
\]

where: \( d_p \) (cm) is the depth penetration into the surface; \( n_c \) and \( n \) are the refractive index values of an ATR crystal and a sample, respectively; \( \theta \) (degree) is the angle of incidence, and \( \lambda \) (cm\(^{-1}\)) is the wavelength of electromagnetic radiation. As shown by eqn. 1, one disadvantage for ATR FT-IR spectroscopy is that the depth of penetration is dependent upon the wavenumber in IR spectra. In an effort to eliminate this effect, we developed an algorithm to obtain the same levels of the depth penetrations across the spectrum. Because eqn. 1 was derived with an assumption that the examined specimens are homogeneous, any composition-concentration variations preclude the use of this useful relationship for quantitative purpose, especially if one is interested in the depth profiling experiments. However, using approach schematically illustrated in Figure 1, it is possible to eliminate the problem. The surface is divided into \( n \) layers with each layer thickness, \( \Theta \). At the each boundary layer, \( \ell \), the response of the sample to local evanescent waves is characterized by a complex refractive index defined by \( \tilde{n}_j = n_j - ik_j \), and \( n_j \) is refractive index, where \( \Theta \) is referred to as the absorption index. By applying a double Kramers-Kronig transform to each layer, which is assumed to be homogeneous, eqn. 1 can be utilized. However, the layers among themselves are not homogeneous, and by stacking all layers together, the surface is reconstructed by a step-wise treatment of volumes occupied by each layer. This approach allows quite accurate quantitative analysis of surfaces and its precision is determined by the number of spectra collected at various depths. Based on this principle, quantitative analysis of the F-A and F-S interfaces can be studied.

Figure 1. A schematic diagram of numerically slicing a nonhomogeneous surface to form a stack of parallel thin homogeneous layers.

Furthermore, by incorporating polarized IR light in an ATR experiment, it is possible to determine orientation of the surface species.
With this background in mind, we will focus on the analysis of the recently developed microwave plasma reactions on polymer surfaces. Such modifications are particularly important for biocompatibility and bioadhesion.

Modification of polymer surfaces using plasma reactions is a continuously growing area of basic and applied research. Because highly energetic plasmas can primarily alter surfaces while still maintaining polymer bulk properties, considerable efforts have been made to analyze surface species created by plasma reactions. While majority of the previous studies concerning plasma reactions focused on the fragmentation of reacting monomeric molecules resulting from the plasma reactions and their chemical attachment to the substrate, in essence, there is no data as to the nature of the substrate sites available for reactions. This issue seems to be of fairly significant importance because the surface reactive sites not only determine if reactions occur, but also how stable newly created surfaces are. We utilized microwave energy to generate plasma that allowed us to react imidazole molecules to crosslinked polydimethylsiloxane (PDMS) surfaces. PDMS is a crosslinked elastomer containing an amorphous SiO₂. For a typical PDMS network, a 0.03 μm particle size amorphous SiO₂ is often used. Because highly energetic plasmas are virtually able to break any bonds, there are at least two possible reaction sites on the PDMS surface:

\[
\begin{align*}
\text{CH₃} & \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{O} & \quad \text{CH₃} \\
\text{CH₃} & \quad \text{Si} \quad \text{O} & \quad \text{Si} \quad \text{O} & \quad \text{CH₃} \\
\end{align*}
\]

or

\[
\begin{align*}
\text{Ar Plasma} & \quad \text{SiO}_2 & \quad \text{SiO}^+ & \quad \text{O}^+ \\
\end{align*}
\]

in which the Si-CH₂⁺ free radical formation results from the hydrogen abstraction, and Si⁺ is generated by the CH₃ cleavage. The formation of SiO⁺ free radicals may result from the Ar microwave plasma reactions of polycrystalline silica. Surface analysis of the microwave plasma reacted PDMS surfaces reveals that not only Si radicals are formed by the methyl group abstraction of the Si-CH₃ groups, but also Si-CH₂ radicals result from the hydrogen abstraction of the Si-CH₃ groups. The Si radicals react with the hydrogen radicals resulting from the hydrogen abstraction of the Si-CH₃ groups, to form SiH species. These reactions are followed by the reactions of the Si-CH₂ radicals with methyl radicals, resulting from a methyl group abstraction of the Si-CH₃ groups, to form Si-CH₂CH₃ species. When imidazole is reacted to the PDMS surface in the presence of Ar microwave plasma, the Si-H groups are not detected on a PDMS surface. On the other hand, the → Si-CH₂-N< species are formed. Imidazole radicals resulting from the hydrogen abstraction of the N-H bonds react with the SiCH₂ radicals, to form Si-CH₂Imidazole entities.

In an effort to facilitate the imidazole-polyurethane (PU) reactions, PU specimens were immersed in a methylene chloride - imidazole solution, followed by an exposure to the microwave radiation using closed and open flow microwave plasma conditions. Physiosorbed imidazole molecules incorporated into PU elastomer networks react with PU surfaces in the presence of Ar plasma, which creates chemically bonded imidazole entities to the PU surfaces through the C=N opening of imidazole and C=O opening of PU, resulting in the C-O-C linkages between PU and imidazole. Although in this particular study the highest concentration of chemically bonded imidazole was obtained at 26.6 Pa Ar pressure and 30 sec. discharge time, it should be kept in mind that other factors may also influence the extent of surface reactions. They may include a soft/hard segment ratio, their free volumes and glass transition temperatures as well as other factors. This part of the presentation will focus on qualitative and quantitative analysis of PDSM, PU, and poly(vinyl chloride) (PVC) polymer surfaces modified using microwave plasma.

**Photoacoustic (PA) Fourier Transform Spectroscopy**

Another powerful method in surface and interfacial analysis is photoacoustic spectroscopy. This method is based on the detection of an acoustic signal emitted from a sample due to absorption of modulated radiation. This is schematically illustrated in Figure 2.

![Image](https://example.com/figure2.png)

**Figure 2.** A schematic diagram of photoacoustic FT-IR setup.

The sample is placed in an acoustically isolated chamber to which a sensitive microphone is attached. On absorption of modulated light, heat is generated within the sample. Its release leads to temperature fluctuations at the sample surface. These temperature fluctuations at the sample surface cause pressure changes in a surrounding gas, which, in turn, generate acoustic waves in the sample chamber. The pressure changes of the gas are detected by a sensitive microphone, and the obtained electrical signal
is Fourier-transformed. In the PAS experiment, the absorbed energy is released in a form of heat that is transferred to the sample surface, and the efficiency of the heat transfer is determined by the thermal diffusion coefficient of the sample, $\alpha_s$ (cm²/s), and the modulation frequency of the incident radiation, $\omega$:

$$a_s = \left(\frac{\omega}{2\alpha_s}\right)^{1/2}$$  \hspace{1cm} (2)

where: $\alpha$ (cm²/s) is the thermal diffusivity; $\omega$ (s⁻¹) is the angular modulation frequency, and equal to $2\pi \nu$ (ν, cm/s, and $\nu$, cm⁻¹, are velocity of mirror and wave numbers, respectively). The thermal diffusion length $\mu_0$ (cm) is related to the thermal diffusion coefficient $\alpha$ through

$$\mu_0 = \frac{1}{\alpha_s} = \frac{2\alpha_s^{1/2}}{\omega}$$  \hspace{1cm} (3)

Based on this relationship, the thermal diffusion length is inversely proportional to the modulation frequency.

Therefore, by changing $\omega$, one changes $\mu_0$, which in effect result in changing the depth from which the acoustic signal is generated. Thus, the capability of surface depth profiling is one of the most appealing features of PA FT-IR. Urban et al. has demonstrated that several applications of PAS in surface depth profiling, and the orientation of the surface species. However, the major drawback of this setup is that the thermal diffuse length also depends on the wavenumber. As a result, the low wavenumber region results deeper penetration depths, and for the high wavenumbers, the spectral information comes from shallower depths. In an effort to eliminate this wavenumber dependence, and obtain a penetration depth wavenumber independent spectra, step-scan photoacoustic FT-IR spectroscopy, can be employed.

The most recent development in the interferometric measurements is so-called step-scan spectroscopy. In this case, a mirror of a Fourier transform interferometer is moved incrementally, and the data are acquired while the retardation is constant. The result is that the Fourier frequency dependence is eliminated. A single frequency of modulation can then be imposed on the IR beam, which applies to all wavenumbers in the spectra. As a result, the photoacoustic sampling depth is constant across the spectrum. Furthermore, using a two-phase lock-in amplifier, in-phase and in-quadrature components of the signal can be simultaneously acquired, and used to obtain the signal phase. Figure 3 illustrates a schematic diagram of the in-phase and quadrature spectra. These advantages are particularly important in understanding molecular level adhesion using a photoacoustic detection.

![Figure 3. Schematic diagram of two components of in-phase and in-quadrature in step-scan phase analysis.](image)

Our recent studies showed that utilization of rheo-photoacoustic stress-strain measurements allows molecular level forces at bilayer interfaces to be monitored. By using the vibrational energy changes resulting from perturbation of the interfacial region, it is possible to correlate the spectroscopic data and the work of adhesion for thermoplastic-thermosetting bilayer systems. Figure 4 illustrates the magnitude of the vibrational frequency changes for several systems.

![Figure 4. Vibrational energy changes resulting from shear forces introduced to the interfacial regions in PDMS/PE, acrylate/PE, acrylate/PP, epoxy/PE, and epoxy/PP (PDMS-polydimethylsiloxane, PE-polyethylene, PP-polypropylene).](image)

The uniqueness of the approach that combines spectroscopic vibrational energy changes and the work of adhesion comes from the fact that it is possible to deconvolute individual contributions to the total work of adhesion. Theoretical foundations were presented elsewhere. In the case of a thermosetting-thermoplastic system, the primary contributors to the work of adhesion are dispersive ($W_a$), repulsive ($W_r$), orientation($W_{or}$), and inductive ($W_i$) energy functions. From these relationships derived for each of the potential energy components, the work of adhesion is given as:

$$W_a = \int F \, dr = \int (F_{in} + F_{out}) \, dr$$

$$= \int (V_{in} + V_{out} + V_{or} + V_i) \, dr = -\int \sigma \, F \, dr$$  \hspace{1cm} (4)

where $F$ represents the ensemble average of the quadratic force over the perturbation coordinates and $\sigma$ is the quadratic force constant of unperturbed substrate.
Figures 5, 6, 7, and 8 show variations of the dispersive, repulsive, orientation, and inductive energy changes for PDMS/PE, acrylic/PE, acrylic/PP, epoxy/PE, and epoxy/PP.

Figure 5. Values of dispersive energy for PDMS/PE, acrylic/PE, acrylic/PP, epoxy/PE, and epoxy/PP.

Figure 6. Values of repulsive energy contributions for PDMS/PE, acrylic/PE, acrylic/PP, epoxy/PE, and epoxy/PP.

Figure 7. Values of orientation energy for PDMS/PE, acrylic/PE, acrylic/PP, epoxy/PE, and epoxy/PP.

Figure 8. Values of inductive energy for PDMS/PE, acrylic/PE, acrylic/PP, epoxy/PE, and epoxy/PP.

Using eqn. 4, the total work of adhesion can be determined. The results are shown below.

<table>
<thead>
<tr>
<th>Bilayer System</th>
<th>Work of Adhesion (J/m²) 10⁻³</th>
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<tbody>
<tr>
<td>PDMS/PE</td>
<td>3.25</td>
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<tr>
<td>Acrylic/PE</td>
<td>1.30</td>
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<tr>
<td>Acrylic/PP</td>
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<td>Epoxy/PE</td>
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<tr>
<td>Epoxy/PP</td>
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References