IR SPECTROSCOPY FOR BONDING SURFACE CONTAMINATION CHARACTERIZATION

Lee H. Pearson

Thiokol Corporation
Advanced Technology
Brigham City, Utah 84302-0707

INTRODUCTION

Organic contaminants such as hydrocarbons and silicones that may be present on bonding surfaces are known to degrade bond strength when cured into the bondline. In-situ characterization of bonding surface contamination is desirable but is somewhat limited by available techniques. Optically Stimulated Electron Emission (OSEE) has been developed and used for qualitative detection of contaminants on some types of surfaces (primarily metals) and infrared (IR) spectroscopy is conventionally used for laboratory evaluation of contamination samples wiped from a bonding surface and dissolved in a solvent. This paper presents an IR external reflection spectroscopy imaging technique for in-situ bonding surface contamination detection and characterization. Methods for optimizing sensitivity to thin organic films are discussed. A discussion of the use of this technique for imaging grease contamination on composite substrate materials is given.

TECHNIQUE DESCRIPTION

IR spectroscopy is an optical technique for evaluating the spectral (frequency or wavelength) content of reflected or transmitted (IR) light. The application of IR spectroscopy to the problem of detection and characterization of surface contamination on SRM bonding surfaces is based on a spectroscopic evaluation of externally reflected IR light from the air - contaminated surface interface. Most contaminants of concern are organic compounds which exhibit mid-IR transmission/reflection spectral signatures that are characteristic of the compound. Such spectral information may be useful in identifying the contaminant type and quantity on the surface. Fig. 1 shows an attenuated total reflection (ATR) spectrum for a typical grease compound, for example. The strong absorption band regions are of particular interest because these are the spectral regions where the grease can be detected in a reflection spectrum. Other organic contaminants such as machine oil, hydraulic oil, and mold release agents exhibit similar characteristic spectra.

Detection of the contaminant film is experimentally accomplished by directing the IR beam reflected from the specimen surface, acquiring a spectrum using a Fourier Transform Infrared (FTIR) spectrometer, and evaluating the spectrum to determine if contamination is present on the surface. An image of surface contamination is obtained by scanning the specimen under the beam in an x-y raster scan manner and obtaining a spectrum at each pixel of the scan. Scale-of-gray or false color images are developed from parameters computed from the spectra. Fig. 2 shows a schematic diagram of the experimental set-up.
Fig. 1. Absorbance spectra for typical grease contaminant.

THEORY FOR ELECTRIC FIELDS IN LAYERED MEDIA

The sensitivity of an IR reflectance measurement to a thin organic contaminant film is dependent upon a number of experimental parameters.
including angle of incidence, polarization of the electric field vector, and wavelength (frequency or wavenumber). Calculations from a theoretical model can eliminate many of the myriad of experimental measurements required to obtain the data needed to optimize experimental parameters. Theory provides insight into the physics of the problem so that a correct physical intuition can be developed which will aid experimental method design and evaluation. The theory used in this work is based on the assumption that the contaminated surface can be modeled as a plane layered media composed of homogeneous, isotropic materials including air, contaminant, and substrate. It is also assumed that sensitivity to a thin contaminant film is maximized by selecting the angle of incidence, polarization, and wavelength such that the electric field intensity in the contaminant film is maximized [1]. The equations used in this work to perform electric field intensity calculations are listed below. (See Ref. 2 for further discussion on electric field theory for layered media.)

The reflection coefficient is defined as the ratio of the reflected electric field amplitude to the incident electric field amplitude. The reflection coefficient for an IR wave reflecting from the interface between two semi-infinite media is given by

\[ r_{12} = \frac{p_1 - p_2}{p_1 + p_2} \quad (1) \]

where

\[ p_j = n_j \cos \theta_j \quad \text{for perpendicular polarization, and} \]

\[ p_j = \cos \theta_j / n_j \quad \text{for parallel polarization.} \quad (2) \]

Similarly, the transmission coefficient is given by

\[ \tan \beta = \frac{2p_1}{p_1 + p_2} \quad (4) \]

where for perpendicular polarization,

\[ t_{\perp} = t_{12} \quad (5) \]

and for parallel polarization,

\[ t_{\parallel} = \frac{n_1 t_{12} / n_2} \quad (6) \]

Perpendicular polarization refers to the case where the electric field vector is perpendicular to the plane of incidence and parallel polarization is for the case where the electric field vector lies in the plane of incidence. The subscript \( E \) refers to the electric field (as opposed to \( H \) for the magnetic induction). For a multilayered media with \( N \) layers including the first and last semi-infinite layers, the reflection and transmission coefficients are given by

\[ r = \frac{(m_{11}^2 + m_{12}^2 N) p_1 - (m_{21}^2 + m_{22}^2 N)}{(m_{11}^2 + m_{12}^2 N) p_1 + (m_{21}^2 + m_{22}^2 N)} = |r| e^{i\phi} \quad (7) \]
where for perpendicular polarization:

\[ t_{E\perp} = t \]  \hspace{1cm} (9)

and for parallel polarization

\[ t_{H\parallel} = t \]  \hspace{1cm} (10)

\[ t_{E\parallel} = \frac{n_{1} t_{H\parallel}}{n_{N}} \]  \hspace{1cm} (11)

The characteristic matrix, \( M \), is given by

\[
M = \left[ \begin{array}{cc}
m_{11} & m_{12} \\
m_{21} & m_{22} \\
\end{array} \right] = \prod_{j=1}^{N} \left[ \begin{array}{cc}
\cos \beta_{j} & -i \sin \beta_{j} / p_{j} \\
\sin \beta_{j} & \cos \beta_{j} \\
\end{array} \right] \]  \hspace{1cm} (12)

where

\[
\beta_{j} = 2 \pi (h_{j}/\lambda) n_{j} \cos \Theta_{j} \]  \hspace{1cm} (13)

\[
n_{j} \cos \Theta_{j} = \left[ n_{j}^{2} - n_{1}^{2} \sin^{2} \Theta_{1} \right]^{1/2} \]  \hspace{1cm} (14)

\[
n_{j} = n + i k = \text{complex index of refraction} \]  \hspace{1cm} (15)

\( h_{j} \) is the \( j \)th layer thickness, \( \Theta_{j} \) is the angle of incidence, \( \Theta_{1} \) is the refracted angle for the \( j \)th layer, and \( \lambda \) is the wavelength in vacuum.

Equations (2) and (3) apply for the respective polarizations for the \( N \)-layer equations as well as the 2-layer equations.

The reflectance, \( R \), is defined as the ratio of the reflected energy to the incident energy and hence, \( R \) represents the fraction of the total energy that is reflected. The transmittance, \( T \), is the fraction of the total energy that is transmitted. The reflectance and transmittance for both polarizations have the form

\[
R = |r|^{2} \]  \hspace{1cm} (16)

\[
T = |p|/|P_{1}| |t|^{2} \]  \hspace{1cm} (17)

where \( r \) is given by Eq. (7), \( t \) by Eq. (8), and \( p \) by Eqs. (2) and (3) for the respective polarizations.

Equations for the electric field intensities are as follows. (Note that the electric field equations assume that the time average square of the incident field is normalized to 1.)

First semi-infinite layer:

\[
\langle E_{E\perp}^{2} \rangle_{x} = 2 \cos^{2} \Theta_{1} [1/2(1+R_{\parallel}) - R_{\parallel}^{1/2} \cos(\phi_{r\parallel} - 4 \pi n_{1} \cos \Theta_{1} / \lambda)] \]  \hspace{1cm} (18)

\[
\langle E_{E\perp}^{2} \rangle_{z} = 2 \sin^{2} \Theta_{1} [1/2(1+R_{\parallel}) + R_{\parallel}^{1/2} \cos(\phi_{r\parallel} - 4 \pi n_{1} \cos \Theta_{1} / \lambda)] \]  \hspace{1cm} (19)

\[
\langle E_{E\parallel}^{2} \rangle_{1} = \langle E_{E\parallel}^{2} \rangle_{1x} + \langle E_{E\parallel}^{2} \rangle_{1z} \]  \hspace{1cm} (20)
\[ \langle E_{\perp 1}^2 \rangle = 2 \left[ \frac{1}{2(1+R_1)} + R_1^{1/2} \cos(\phi_{\perp 1} - 4\pi n_1 \cos \theta_1 / \lambda) \right] \]  

(21)

Last semi-infinite layer:

\[ \langle E_{\parallel \perp}^2 \rangle = \frac{\gamma_N}{f_N} t_{E\parallel} \left| e^{-4\pi \text{Im}(\gamma_N) / \lambda} \right|^2 \]  

(22)

\[ \langle E_{\parallel z}^2 \rangle = \frac{n_1 \sin \theta_1}{f_N} t_{E\parallel} \left| e^{-4\pi \text{Im}(\gamma_N) / \lambda} \right|^2 \]  

(23)

\[ \langle E_{\parallel N}^2 \rangle = \langle E_{\parallel \perp}^2 \rangle + \langle E_{\parallel z}^2 \rangle \]  

(24)

\[ \langle E_{\perp N}^2 \rangle = \left| t_{E\perp} \right|^2 e^{-4\pi \text{Im}(\gamma_N) / \lambda} \]  

(25)

\( k_{th} \) Middle layer:

\[ Q_k(z) = \begin{bmatrix} U_k(z) \\ V_k(z) \end{bmatrix} = N_k(z) \prod_{j=k}^{N-1} Q_{N-1}^{j} \]  

(26)

\[ Q_{N-1} = \begin{bmatrix} U_{N-1} \\ V_{N-1} \end{bmatrix} \]  

(27)

\[ N_k(z) = \begin{bmatrix} \cos \alpha_k \\ \sin \alpha_k \end{bmatrix} \begin{bmatrix} -ip_k \sin \alpha_k \\ \cos \alpha_k \end{bmatrix} \]  

(28)

\[ \alpha_k = 2\pi \gamma_k (z-z_{k-1}) / \lambda \]  

(29)

\[ \gamma_k = n_k \cos \theta_k = \text{Re}(\gamma_k) + i \text{Im}(\gamma_k) \]  

(30)

where for parallel polarization

\[ Q_{N-1} = \sqrt{2} n_1 \begin{bmatrix} t_{H\parallel} \\ p_{N-1}^* \end{bmatrix} \]  

(31)

\[ \langle E_{\parallel \perp}^2 \rangle = 1/2 |V_k(z)|^2 \]  

(32)

\[ W_k(z) = n_1 \sin \theta_1 U_k(z) / f_k \]  

(33)

\[ \langle E_{\parallel z}^2 \rangle = 1/2 |W_k(z)|^2 \]  

(34)

and for perpendicular polarization

\[ Q_{N-1} = \sqrt{2} \begin{bmatrix} t_{E\perp} \\ p_{N-1}^* \end{bmatrix} \]  

(35)

2021
The $\langle E_k^2 \rangle$ brackets refer to the time averaged electric fields. The total energy present in a thin layer is proportional to the integral of the intensity of the electric field in the layer and is expressed as

$$\text{Energy} \sim \int \langle E_k^2(z) \rangle \, dz \quad (37)$$

The optical properties are $n$ and $k$ (see Eq. (15) above) and are called such whether they are measured at optical (visible) wavelengths, ultraviolet (UV), or IR wavelengths. $n$ is the real part of the complex index of refraction and is commonly referred to as the index of refraction and $k$ is the imaginary part of the index of refraction and is called the extinction coefficient. $k$ is non-zero for media that absorb electromagnetic radiation. For organic compounds, both $n$ and $k$ vary considerably with wavelength in the infrared spectral regions near absorption bands. In order to perform calculations using the theory for a layered media outlined above, $n$, $k$, and $h$ (thickness) are needed for each layer. Methods to measure optical properties are found in numerous places in the literature. (See Refs. 3-5 for methods used in this work.)

Using the assumption that the sensitivity of the reflected signal to the presence of a thin contaminant film is maximized by maximizing the electric field energy in the film, the polarization, angle of incidence, and wavelength of the incident IR wave are varied until the field is maximized. Computer calculations were made to aid in this process. Using the equations listed above, calculations of the electric field intensity were performed for an air-grease-carbon phenolic layered system for a grease thickness of 0.3 microns and using measured optical properties for both the grease and the carbon phenolic. The computer program was written to find the wavelength and angle of incidence that maximized the parallel and perpendicular polarized components of the energy in the contaminant film. The calculations show that the electric field energy is maximized by parallel polarizing the light and directing it at an angle of incidence of approximately 47 degrees with a wavelength of approximately 7 microns. Fig. 3 shows a plot of the integral in Eq. (37) versus the angle of incidence for $\lambda=7$ microns for both parallel and perpendicular polarizations.

**DATA ANALYSIS**

The data obtained by FTIR instrumentation are subject to noise and signal offsets resulting from changing alignment. For low levels of contamination, signal changes are difficult if not impossible to see by visual comparison of spectra because of noise and offset. Use of elementary signal processing methods can show surprising improvement to low level signal change detectability.

To reduce noise, averaging of spectra and smoothing have been employed in this work. Spectra averaging is performed by the FTIR spectrometer software by taking $N$ consecutive spectra and computing their average. ($N=32$ to $64$, typically gives good results.) Smoothing is performed by piece-wise fitting a second order polynomial to the spectral data using a least-squares method or by performing an $N$-point ($N=3,5,7,9,...$) moving average. Both smoothing methods have been found to give virtually the same results, but the latter is computationally much faster.

Offset is generally caused by slight changes in optical alignment from measurement to measurement and can be eliminated or substantially
Theoretical calculations of integral of \( \langle E^2 \rangle \) fields in grease contaminant layer for air-grease (0.3 microns)-carbon phenolic system at 6.99 micron wavelength reduced by taking the derivative of the spectrum with respect to wavelength or wavenumber. Another method to reduce offset is accomplished by: 1) obtaining the reflectance at the wavelength for a characteristic absorption band peak, 2) obtaining the reflectance at a wavelength at the edge of the absorption band, and 3) dividing or taking the ratio of the two reflectances.

**IMAGING RESULTS**

A carbon phenolic plate was contaminated with four 1.0-inch diameter spots of grease (5.4, 11.3, 23.9, 48.9 mg/ft²). The plate was placed on an x-y scanning table and raster scanned under the beam of the FTIR spectrometer. A spectrum was taken every 0.25 inch in both x and y over an area of 2.5 inches x 9.0 inches. Images were generated by plotting as a scale of gray the ratio value as calculated using the procedure listed above and by plotting the peak value of the derivative in the absorption band region. The results are shown in Figs. 4a and 4b, respectively. Figure 4c was obtained by simple peak detecting the absorption band. No attempt was made to remove offset. The spectra were taken at an angle of incidence of approximately 30 degrees using the unpolarized beam from the spectrometer and a reflectance attachment similar to that illustrated in Fig. 2. Even though the experiment was not fully optimized, all levels of contamination are detectable, although, the lowest level is somewhat difficult to see in the image.

**CONCLUSIONS**

Theoretical calculations indicate that oblique incidence parallel polarized light should be used to maximize sensitivity to thin
contaminant films. Simple signal processing methods which remove spectrum offset were found to be effective. Experimental results shown in this work lend credibility to the potential of IR reflection spectroscopy as an imaging method for detection of bonding surface contamination. The spectroscopic nature of the technique leads to strong potential use of the technique to not only detect but to identify contaminant types. The technique also lends itself to physical modeling which can strengthen its quantitative capabilities.

ACKNOWLEDGMENT

Thanks and appreciation are extended to Dr. Wilford N. Hansen at Utah State University for supplying some of the data and physical concepts used to support this work. Also, appreciation is extended to Danny G. Gill for many hours of tedious laboratory work.

REFERENCES