Characterization of Epoxy Coatings on Steel by Reflection / Absorption Fourier Transform Infrared Spectroscopy. I. Effects of Film Thickness and Angle of Incidence

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Synopsis

Films of amine-cured epoxy coating of varying thicknesses from 100 Å to 2.5 μm on steel have been studied by reflection/absorption Fourier transform infrared spectroscopy (FTIR-RA). The shape and frequency of several strongly absorbed bands of epoxy have been examined as a function of film thickness and angle of incidence. Compared to transmission spectra, reflection/absorption spectra of epoxy coating on steel show band shifts and distortions of the bands at 1510, 1247, and 1040 cm^{-1}. These effects are more pronounced at increased thickness and at grazing angles. For thin films (< 100 nm), RA spectral intensity increases with increasing angle of incidence. For thicker films, the relationship is quite complex. The relationship between film thickness and FTIR-RA spectral peak height of an amine-cured epoxy coating on steel has also been established.

BACKGROUND

Reflection/absorption infrared spectroscopy, commonly referred to as external reflection infrared spectroscopy, has become a powerful, nondestructive technique for studies of thick and thin films on metal surfaces.[1] This technique, which is illustrated in Figure 1 for both single and multiple reflections, was developed by Francis and Ellison[2] and Greenler and co-workers.[3-5] In reflection/absorption infrared spectroscopy (RAS), one measures an absorption band of a surface film by measuring the change of the substrate reflectivity, ΔR, due to the surface film, as approximated by:[6]

$$\Delta R = 1 - \frac{R}{R_o} = \frac{16\pi \, dk \sin^2\theta}{\lambda n^3 \cos\theta} \tag{1}$$

where R and R_o are the reflectivity of the substrate with and without a film, λ is the wavelength, d and n are the thickness and refractive index of the film, and θ is the angle of incidence. k is the extinction coefficient, defined by $k = \lambda\alpha/4\pi$, where α is the absorption coefficient of the film.

When infrared radiation strikes a polished metal surface, an electric field is generated near the surface. Reflection/absorption spectroscopy (RAS) theory indicates that the maximum infrared (IR) signal is obtained when the electric
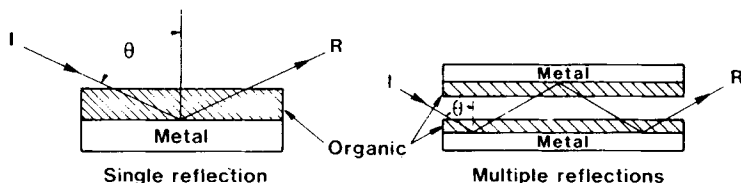
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Fig. 1. Single and multiple reflection set-up of the reflection/absorption experiment.

field is highest. This is achieved when the incident light is at large angles of incidence (θ = 75–89°). There is very little interaction between the beam radiation and the sample for a normal incidence beam or for perpendicular polarized light at all angles of incidence. For parallel polarized radiation, only dipole moments of the surface species that are normal to the metal surface interact with the electric field to produce the IR absorption bands. This selection rule can be used to study the orientation of adsorbed molecules on metal surfaces.[2,6] RAS can be used for studies of both thin (monolayer) and thick films (> 1000 nm). Under optimal conditions, an RA spectrum of a thin film on a metal can be 25 times stronger than the corresponding transmission spectrum of the same film on a transparent substrate.[4] For thick films, a single reflection and angles of incidence of between 45° and 75° are sufficient.

Reflection/absorption spectroscopy is a complicated experimental technique. The intensity and shape of the absorption bands obtained by this technique are different from those obtained by the conventional transmission technique, and are a complex function of numerous parameters.[7] While studying the corrosion-related degradation of both thin and thick protective coatings (epoxy, polyurethane, polybutadiene, and acrylic) on cold-rolled steels using RAS in combination with Fourier transform infrared spectrometry, we observed frequency shifts and distortions (with respect to transmission spectra) of strong absorption bands of these coatings. Verification of these effects are important in studies of protective coatings on metals. Knowing these effects will help to understand the chemical and structural nature of surface coatings before and after exposure to degradation environments. It will also help to accurately assign RA spectral absorption bands of materials whose library spectra existed only in the transmission mode.

Unfortunately, studies on this subject have been few. Greenler and co-workers,[5] using incident angles between 84 and 89 degrees and parallel polarization, have observed a shift of 32 cm^{-1} (to higher frequency) of Cu_2O on Cu when changing from transmission to the reflection mode. Their calculations (but no experimental data) also showed no band shifts for a moderately strong absorption band, such as the 1035 cm^{-1} of liquid benzene (k = 0.07). Based on these calculations, they suggested that the "position of moderately strong bands in the RA spectrum should agree with their positions in a transmission spectrum." Using RAS connected to a Fourier transform infrared spectrometer, Allara et al.[9] have shown, both theoretically and experimentally, band distortions and shifts of the C=O band of poly(methyl methacrylate) (PMMA) films ranging from monolayer to 2 μm thickness on gold substrates. Harrick[7] also provided several examples showing the effects of

optical constants on band shapes and intensities of RA spectra of polymer films on metal substrates.

Since understanding of the effects of variables on RA band shapes applies specifically for certain film/substrate systems, it was important to investigate these effects for the epoxy-steel system used in this study. In this paper, the effects of film thickness and angle of incidence on the spectral characteristics of epoxy coatings on cold-rolled steel obtained by reflection/absorption Fourier transform infrared spectroscopy (FTIR-RA) are reported. The effects of steel substrates, surface roughness, and state of polarization on FTIR-RA spectra will be reported in a later paper.

EXPERIMENTAL PROCEDURE

Materials and Specimen Preparations

Materials

The resin used was a low molecular weight, solid epoxy (Epon 1001 F)* derived from bisphenol A and epichlorohydrin having the following structure
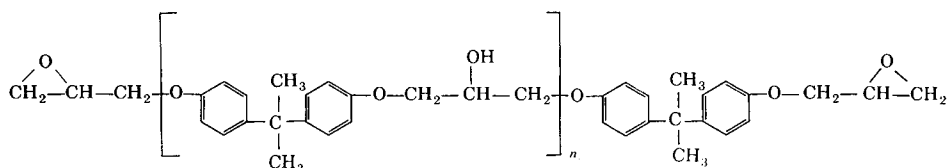
where the average value of n is 2. The epoxy coating was prepared from a formulation containing 100 parts of epoxy, 6 parts of diethylenetriamine (DETA; curing agent), and 3 parts of butylated urea formladehyde (flow-controlling agent). The epoxy resin and flow-controlling agent were mixed together as the base component which was mixed with the curing agent just before applying the coating to the substrate. Resin solutions in ethylene glycol/toluene (50/50, w/w) were prepared at concentrations ranging from 0.5 to 33%. The substrates were 25 × 25 mm, low-carbon SAE 1010, cold-rolled steel plates. NaCl plates of 25 mm diameter were also used in this study.

Specimen Preparation

The steel specimens were mechanically polished (final polishing was with 0.25 μm alumina powder), rinsed repeatedly with water, rinsed with methanol, blown dry with hot air ($\sim 80\,^\circ$C) and stored in a desiccator containing $CaSO_4$ before use (but not more than 3 days). The cleaning procedure was repeated immediately prior to the coating application. NaCl plates were ground and polished in the usual manners for IR transmission spectroscopy. The coating was carried out by placing the substrates on a platform, flooding with resin solutions, and spinning them horizontally at 3500 rpm for 30 sec using a

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*Trade names are given solely to indicate experimental materials and equipment used and not meant to recommend a particular product.
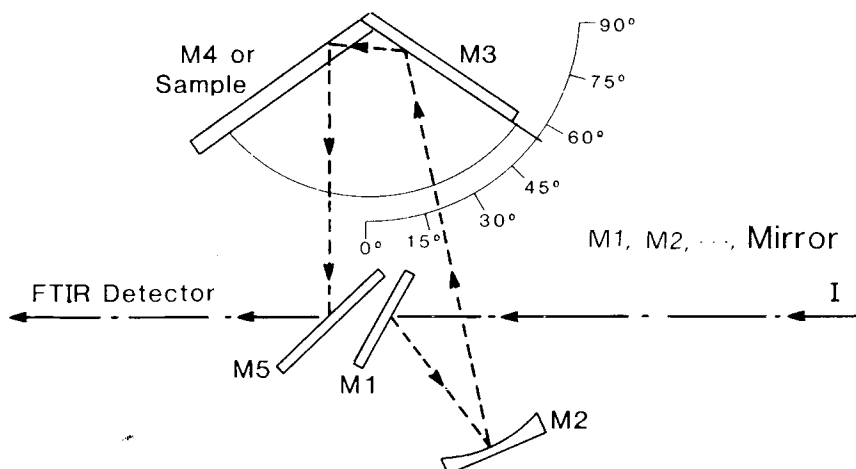
Fig. 2. Optical layout of the FTIR-RA experiment.

photoresist spinner. All specimens were air-cured at room temperature (in a closed cabinet) for two weeks, and placed in a vacuum chamber at 625 mmHg for an additional two weeks. Film thicknesses were measured using a scanning spectroscopic reflected light microscope which measured the reflected light spectrum in the 400–700 nm range (Nanometrics). For films of less than 50 nm, the measurements were also made using an ellipsometer. The values given were the average of three measurements on each sample.

A free film of the amine-cured epoxy coating was also prepared by spin coating the 38% solution on a 25-mm diameter tin foil disc. After air-curing for 3 weeks at room temperature, the coated disc was immersed in a room temperature water bath. The film was readily separated from the disc and floated off after approximately 30 minutes of immersion. After wiping off excess water, the free film was stored in the vacuum chamber, then desiccator, before collecting the spectrum.

Reflection / Absorption Fourier Transform Infrared Spectra

Spectra were obtained using a 60 SX Nicolet FTIR spectrometer and a Barnes variable angle specular reflection accessory. The experiment set-up is shown in Figure 2. The spectrometer was equipped with a liquid nitrogen-cooled mercury cadmium telluride detector and was constantly purged with dry air to minimize the effect of moisture. The instrument was also equipped with a laser reference interferometer to insure wavelength accuracy. All spectra were the result of 1000 coadditions and were taken at 4 cm^{-1} resolution. Single reflection at specified angles of incidence was employed for FTIR-RA analysis. Peak frequencies were recorded by the computer, and shoulder frequencies were located visually after optimal expansion. Except for the transmission spectra which were ratioed against the background, all FTIR-RA spectra have been ratioed against the spectrum of a silver reference mirror. All spectra are shown in the absorbance mode.
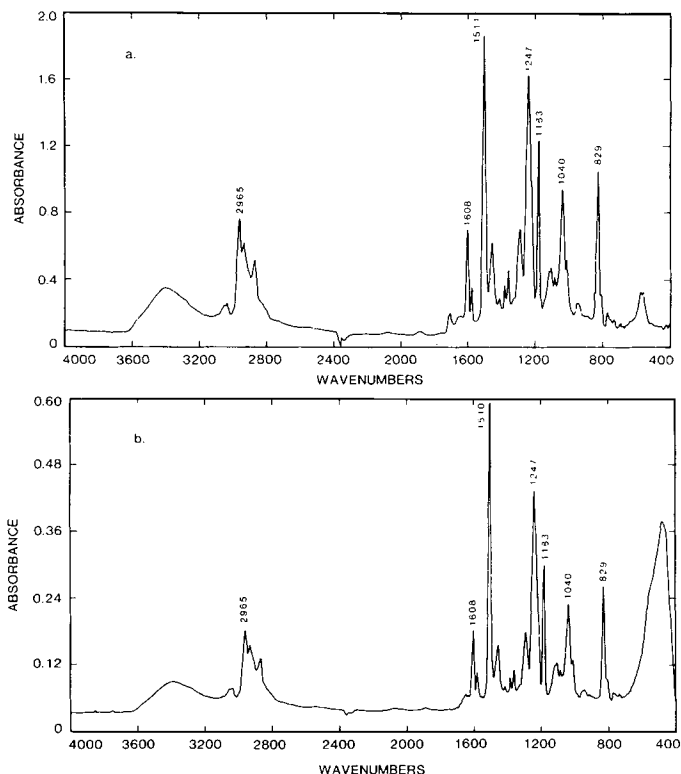
Fig. 3. FTIR-transmission spectra of amine-cured epoxy coating. (a) free film; (b) film on NaCl crystal.

RESULTS AND DISCUSSION

FTIR-RA Spectra of Amine-Cured Epoxy Coatings on Cold-Rolled Steel

Transmission and FTIR-RA spectra of an amine-cured epoxy coating on cold-rolled steel are shown in Figures 3 and 4. The coating thicknesses were 2.49 μm on steel and 2.50 μm on NaCl. The thickness of the free film was not measured. Band assignments of the amine-cured epoxy-free film and coating on cold-rolled steel were presented previously.[8] The transmission spectrum of epoxy coating on NaCl crystal is identical to that obtained from a free film (Fig. 3) and, except for a small difference of the C—O peak frequency (1035–1041), it is very similar to those obtained by Yoshida and Ishida[10] for the lower molecular weight, amine-free epoxy resin (Epon 828). Comparing Figures 3 and 4, there are differences in band shapes and band maximum frequencies at the 1510, 1247, and 1040 cm^{-1} peaks (from Fig. 3) between the spectra obtained by the RA technique and those by the transmission technique. This is in agreement with similar observations by Allara et al.[9] for the C=O band of PMMA films on gold substrate. They also noted that strongly absorbing groups such as C=O and C=N can lead to significant shifts in peak maximum frequencies. In this paper, we will examine only those strong
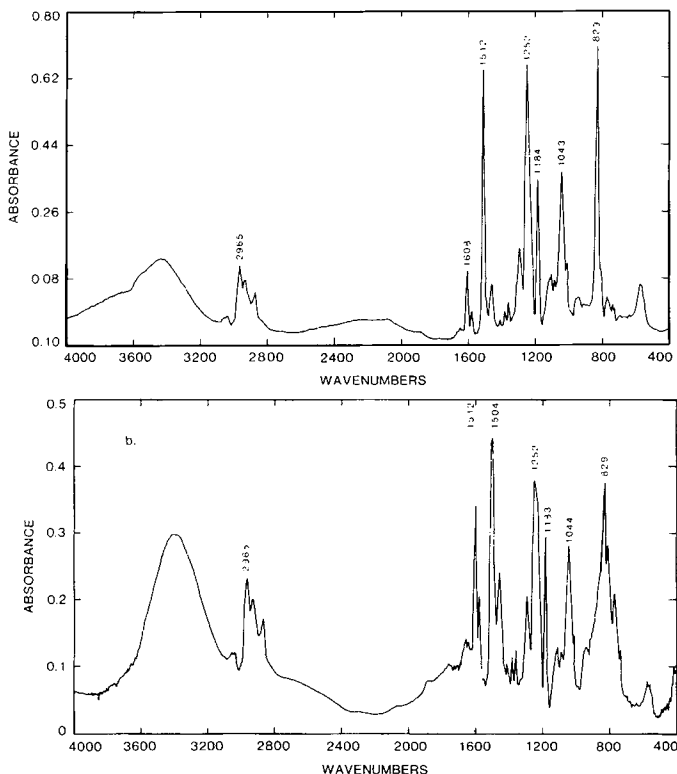
Fig. 4. FTIR-RA spectra of amine-cured epoxy coating on cold-rolled steel substrate. (a) at 40°; (b) at 84°.

absorption bands (high extinction coefficient), namely, 1510, 1247, 1183, 1040, and 829 cm^{-1} bands in the spectrum of the amine-cured epoxy coating.

The extinction coefficient (k) of the organic film can be estimated from the equation

$$I/I_o = e^{-4\pi k \, d\nu} \qquad (2)$$

where I/I_o is the fraction of power transmitted through the sample, d is the film thickness in cm, ν is the frequency in cm^{-1}. Applying Eq. (2) to the transmission experiment at normal incidence with epoxy film on NaCl plates, approximate values of k were calculated for several absorption bands; these

TABLE I
Extinction Coefficient and Half Band Width of Several Adsorption
Bands of Amine-Cured Epoxy Coating

Frequency, ν (cm^{-1})	Transmittance	k	$\nu_{1/2}$ (cm^{-1})
1510	.2812	.2674	13.38
1247	.3664	.2563	37.22
1183	.5585	.1569	15.94
1040	.6607	.1269	36.99
829	.5470	.2317	21.04

are presented in Table I. Table I also includes the half band width, $\nu_{1/2}$. It is evident from Table I and Figures 3 and 4 that the RA spectral band distortions of epoxy coating on steel are dependent upon k and $\nu_{1/2}$ values.

Coating Thickness and FTIR-RA Spectra of Amine-Cured Epoxy Coatings on Cold-Rolled Steel

Calibration Curve

Equation (1), which expresses the change in reflectivity of a metal surface due to the presence of a polymer film, is only an approximation. The exact theoretical treatments of this relationship are very complicated, even for normal incident radiation.[11] The relationship between band intensities of an RA spectrum and film thickness does not follow the absorption law.[5,11,12] McIntyre and Aspnes, using linear-approximation theory for a strongly absorbing film on a metallic substrate at 45° incident angle, have shown that the linear relationship between ΔR and film thickness wavelength ratio (d/λ) is only valid when d/λ is very small, for example, $d/\lambda \leq 0.01$ for perpendicular polarization, and $d/\lambda \leq 0.03$ for parallel polarization. Thus, for quantitative studies, calibrations must be done for each set of of variables employed, such as metal substrate, coating type, angle of incidence, wavelength, and state of polarization.

A calibration for two band positions of DETA-cured epoxy coating on cold-rolled steel is shown in Figure 5. There appears to be good linearity between peak height and film thicknesses of up to 70 nm. Allara[12] also showed
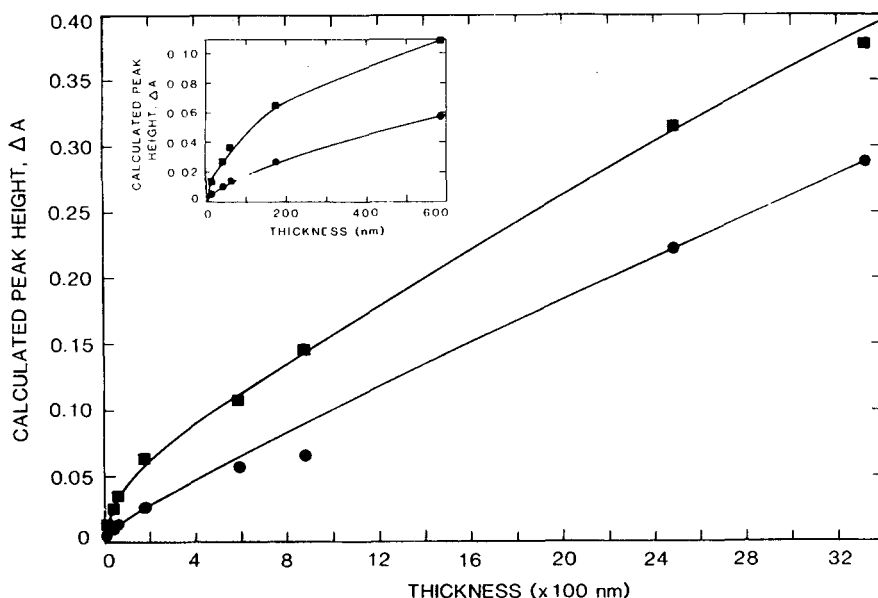

Fig. 5. Relationship between the peak height of the FTIR-RA spectrum of the amine-cured epoxy on cold-rolled steel and the film thickness, (84° incident angle). (a) -■-■-■-, C=C stretching of the benzene ring at 1510 cm^{-1}; (b) -●-●-●-, out-of-plane bending of the p-disubstituted benzene ring at 829 cm^{-1}.

a similar relationship between the log R/R_o (reflectance with film/reflectance without film) and film thickness of poly (1-butene) on Cu with good linearity up to 30 nm and 50 nm for the 2915 and 1465 cm^{-1} bands, respectively. Yoshida and Ishida[10] also showed a similar curve to those of Figure 5 for the 2925 cm^{-1} band of undecylimidazole on Cu, with linearity up to 80 nm. However, they reported a linear relationship between peak height of the 1511 cm^{-1} band and film thicknesses up to 200 nm of a low-molecular weight epoxy resin on copper.

Effects of Film Thickness on FTIR-RA Spectral Characteristics of Amine-Cured Epoxy on Cold-Rolled Steel

Figure 6 shows FTIR-RA spectra, in several regions of the DETA-cured epoxy films on steel of thickness ranging from 10.0 nm to 2.49 μm. All spectra were taken at an angle of incidence of 84° using unpolarized light. Figure 6 shows considerable changes of spectral characteristics of epoxy coatings as a result of change in film thickness. For example, near the 1512 and 829 cm^{-1} bands there are two well-resolved peaks at the 10 nm thickness. As the thickness increases, the smaller peaks become less visible, until completely overlapped at 173 nm. In addition to these overlappings, the bands at 1512 and 1252 cm^{-1} are highly distorted at 2.49 μm thickness. On the other hand, a new peak near 808 cm^{-1} is visible at 874 nm and becomes very pronounced at 2.49 μm.

FTIR-RA spectra at different coating thicknesses help to distinguish the frequency shifts due to changes in optical constants (refractive index n and extinction coefficient k) and those due to changes in thickness. Comparing the FRIR-RA spectra of thin films ($\leq$ 173 nm, Fig. 6) with transmission spectra (Fig. 3), it is shown that, except for the peak maximum of the band at 1247 cm^{-1}, which shifted 5 cm^{-1} to higher frequency, most band frequencies are identical between the spectra of the two techniques. The observed shift at the 1247 cm^{-1} band is in agreement with the general conclusions made by Allara et al.[9] that, for very thin films, and at grazing angles of incidence, the shifts are always to higher frequencies; and that these shifts are several times less for sharp bands ($\nu_{1/2} \leq 5$ cm^{-1}) than for broad bands ($\nu_{1/2} \sim 20$ cm^{-1}).

Since band shapes could be described by optical theories,[4] the frequency shifts of the reflection spectra of thin films (with respect to transmission spectra) can be predicted by the relations between reflectivity or transmissivity of a multilayer sample and the system variables. These have been theoretically and experimentally demonstrated for several film substrate systems.[5,9] Allara et al.[9] observed a shift of 9 cm^{-1} for the C=O band ($k = 0.36$) of PMMA film on gold when changing from the transmission to the reflection mode at 82°. Greenler et al.[5] reported a shift of 32 cm^{-1}, from 623 cm^{-1} in the transmission mode to 655 cm^{-1} in the multiple reflection mode at angles of incidence between 84 and 89° of a Cu_2O ($k = 5$) film on copper. These shifts to higher frequencies of thin films were attributed to the optical effects of the film. Similar explanations were given by Harrick[7] for frequency shifts and band distortions of Mylar films on aluminum surfaces. Based on these references, the observed shift to higher frequencies for the 1247-cm^{-1} band of thin epoxy films on cold-rolled steel may be assigned to optical effects (k and n). The effects of n and k on RA spectra are given below.
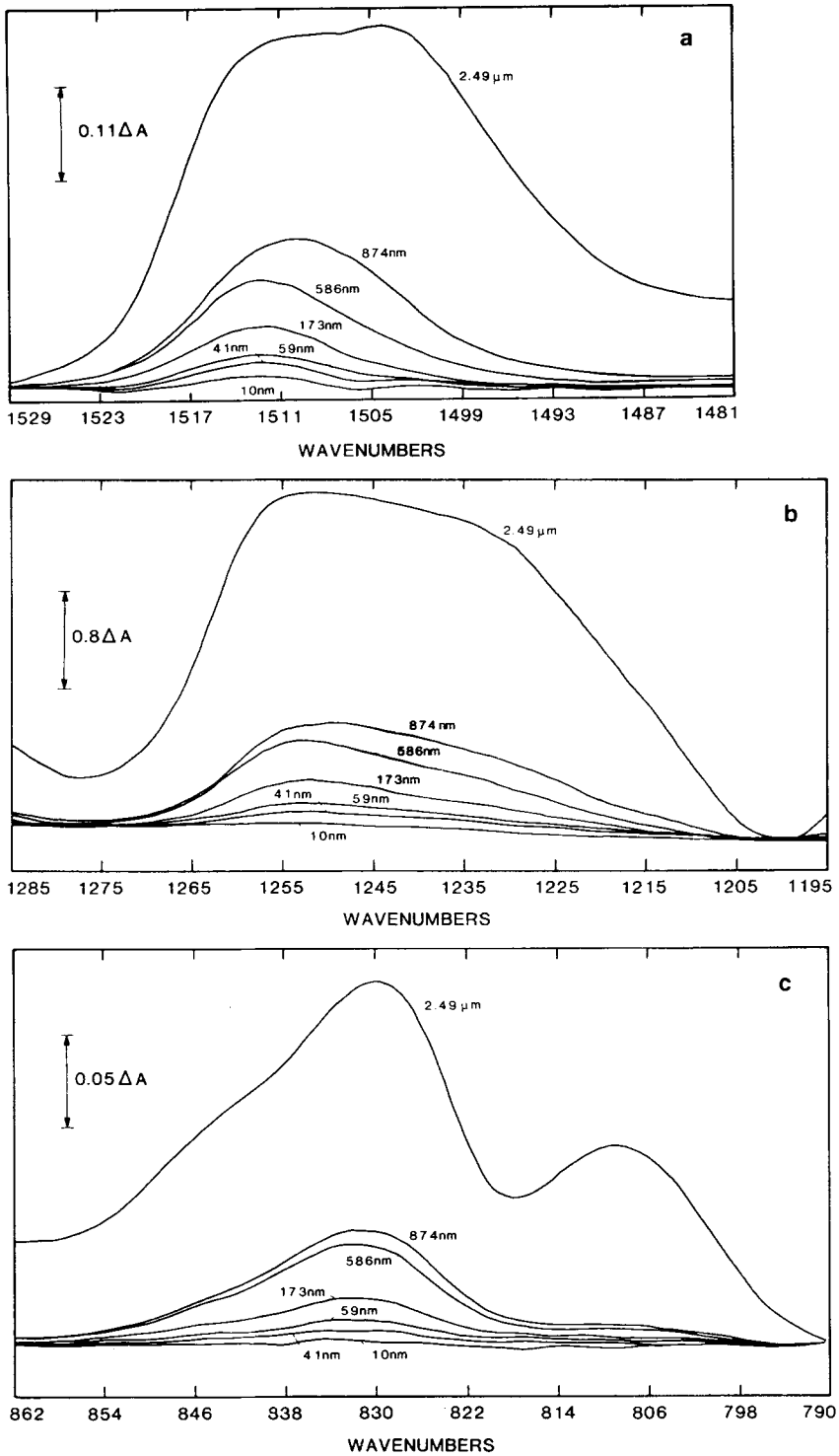
Fig. 6. FTIR-RA spectra in several regions of amine-cured epoxy films on cold-rolled steel at different thickness (unpolarized light at 84° incident angle). (a) 1530–1480 cm^{-1}; (b) 1285–1195 cm^{-1}; (c) 860–790 cm^{-1}.
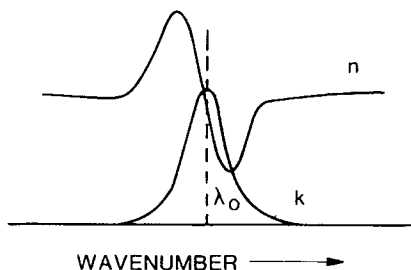
Fig. 7. Typical variation of n and k as a function of frequency near an absorption band.

Although the actual distributions of n and k as a function of frequency were not determined in this study, it is well known that k follows a Gaussian function going through the maximum, and n follows an anomalous dispersion, changing rapidly at the band maximum (Fig. 7). This dispersion will likely result in an asymmetry, particularly at high angles of incidence, in the absorption band recorded by the reflection technique. This phenomenon has been observed and discussed in detail for internal reflection spectroscopy.[13] On the other hand, the displacement to higher frequency can be explained by the optical theory of external reflection technique. Although n and k are related to each other by a complex function, the absorption intensity increases as the refractive index decreases.[13] The slope of this relation is steeper at very high angles of incidence.[4] As seen in Figure 7, the absorption will be stronger at higher frequency (low n); thus, the shifts due to n or k of thin films will be to a higher frequency.

The second effect in band distortions of a film on metal involves the phase shift between the incoming and reflected beams.[4] The size of the phase shift, which determines the magnitude of the electric field formed at the metal surface, is dependent on the angle of incidence and the optical constants of the system. For parallel polarization and at high angles of incidence, the phase shift changes rapidly and produces a sizable electric field (E) as discussed earlier. Thus, ultrathin films (monolayer or less) can be observed under these conditions. The E value varies periodically with a repeated distance, $f = 1/2\nu n \cos \theta'$ (9), where θ' is the angle of incidence at the metal surface. It can be seen that E at any fixed distance from the surface will differ for different frequency regions and the energy absorbed will be controlled by n. This generally gives rise to asymmetry at opposite sides of a reflection band.

Another factor in band distortions and shifts in RA spectra is that the incident beam reflects from the front surface of the film. This reflection is dependent on both n and k, and for constant or negligible values of k, will increase with increasing n.[13] Therefore, less light will be reflected from the front surface in the low region of n in the dispersion curve. This will cause distortions in the RA spectra and this distortion will also result in a shift toward higher frequencies.

As the film thickness increases to the micrometer range, the distortions and band splittings of an epoxy film on cold-rolled steel are more apparent as seen in the 1510 and 1247 cm^{-1} bands. Increases in thickness also result in a shift to higher frequency of the 1040 cm^{-1} band. Greenler et al.[5] predicted a band splitting for a Cu_2O film on Cu at 420–1200 nm, but this was not observed

experimentally. On the other hand, Allara et al.[9] showed good agreement between the calculated and experimental band splitting of the carbonyl band of a 1.45 μm PMMA on gold, taken at 82° angle of incidence. Thus, the theory allows a qualitative description of distortion effects in reflection spectra for both thin and thick films.

In addition to the effects of optical constants, surface reflectivity, and phase shifts, other optical phenomena such as interference fringe and optical cavities influence the IR spectral characteristics of thick films on metals.[7] Harrick[13] has detailed the effects of these factors on band shapes of IR spectra obtained by internal reflection spectroscopy.

Angle of Incidence and FTIR-RA Spectra of Amine-Cured Epoxy Coating on Cold-Rolled Steel

Figures 8 and 9 show the band shapes and intensities of amine-cured epoxy coatings on cold-rolled steel of different film thickness at various angles of incidence. For a thin film, the band intensities become pronounced at high angles of incidence as predicted by the theory.[4] This phenomenon occurs at grazing angles of incidence only because the component of the electric field normal to the surface has sufficient amplitude to interact with the film and produce an observable spectrum. The other component of the electric field, which is parallel to the surface plane, is very small at the interface and will not give rise to an observable signal. The theory seems to hold up to 200 nm of epoxy/steel system for the low frequency region. For high frequencies and thicker films, e.g., Figs. 8(b), (c), and 9(b), (c), the relationship between intensity and angle of incidence is quite complex. In general, for thick films the intensities decreases as θ increases.

This could be explained by the multiple reflection components of an incident beam striking at a metal surface covered with an organic film (Fig. 10). The observed intensities are

$$I_{obs} = I_1 + I_2 + I_3 + I_4 + I_5 + \cdots$$

I_6 and higher orders of reflection can be neglected because their intensities are very small. As the thickness, hence the effective pathlength ($d/\cos \psi$), increases, I_{obs} decreases because the radiation transmitted into the film is absorbed more before reflecting at the rear surface. Since ψ is proportional to θ, I_{obs} will decrease as θ increases as observed in Figures 8(c) and 9(b) and (c).

As film thickness becomes large, the contributions of I_2, I_3, I_4, and I_5 will be less, and the intensity due to surface reflection of the coating, I_1, becomes significant to the I_{obs} of the RA spectrum. The reflection coefficient, r, which is the ratio of the reflected to the incident intensities, is given approximately by the expression:[13]

$$r = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}$$

Although the above equation is correct for normal incidences ($\theta = 0$), it is approximately correct for angles of incidence as large as 45° for unpolarized light. Using k in Table I and $n = 1.56$,[15] r values of an amine-cured epoxy
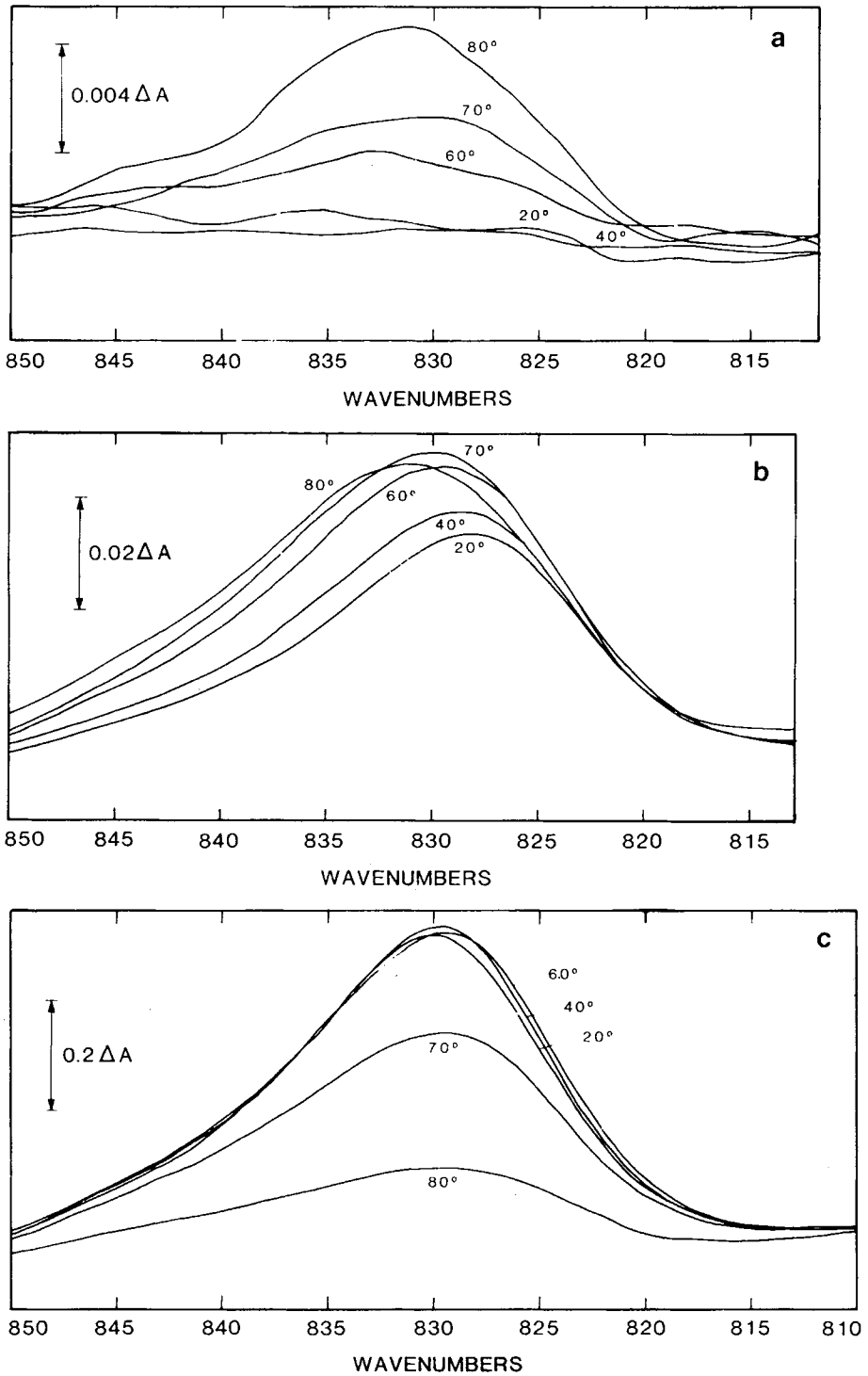
Fig. 8.   FTIR-RA spectra for several thicknesses of amine-cured epoxy on cold-rolled steel at different incident angles in the 850–810 cm^{-1} region. (a) 59 nm; (b) 874 nm; (c) 2.49 μm.
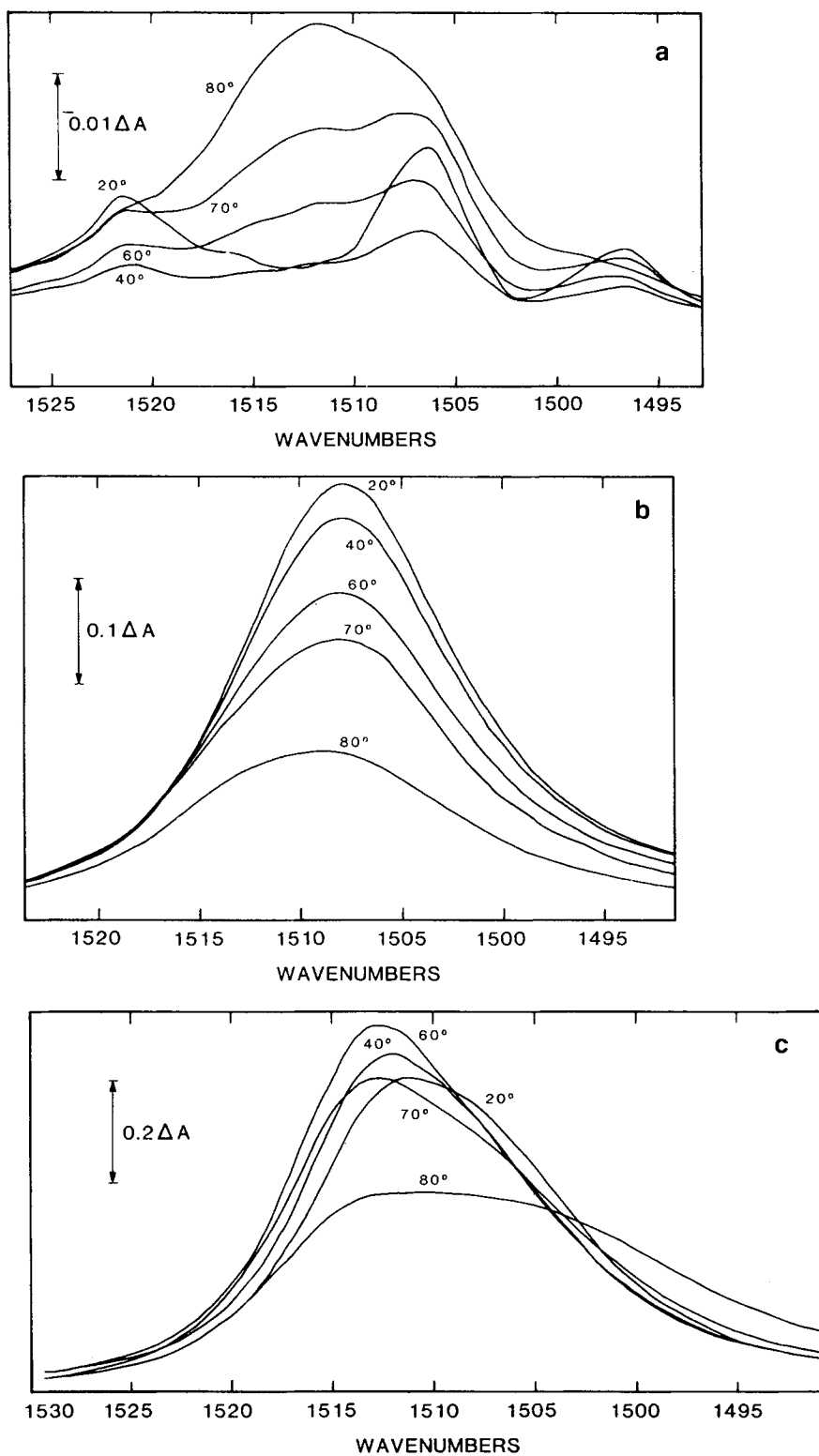
Fig. 9. FTIR-RA spectra for several thicknesses of amine-cured epoxy on cold-rolled steel at different incident angles in the 1530–1480 cm^{-1} region. (a) 59 nm; (b) 874 nm; (c) 2.49 μm.
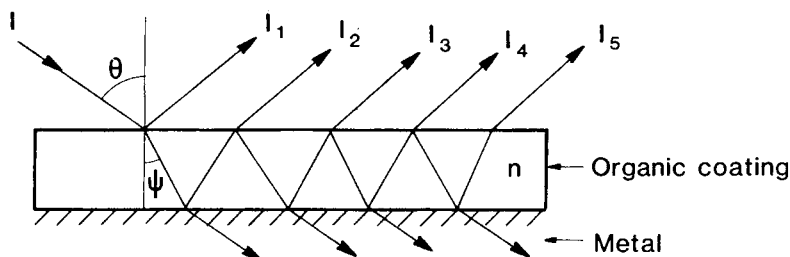
Fig. 10. Multiple components of light by reflection at the front and back surface of a film on metal substrate.

coating at the 1510 and 829 cm^{-1} bands are approximately 0.058 and 0.055, respectively. These low values of r at low angles of incidence may explain the anomalies observed for the 20 and 40 degrees in Figures 8(c) and 9(c).

In addition to intensity change as a function of θ and film thickness, Figures 8 and 9 also show peak maximum shifts and distortions as the result of changes in θ. Bates[14] observed similar shifts. Such shifts are also very pronounced for the internal reflection technique especially when θ is near the critical angle.[13] These shifts could be explained by the same factors discussed earlier for film thickness, and reflection technique since reflectivity (both front and back surface) is controlled by the refractive index and angle of incidence as given by the well known Fresnel's equations. It is also evident from Figures 8 and 9 that RA bands are sharper and less distorted at lower angle of incidence. Thus, for rather thick films (> 100 nm), angles between 40 and 75 degrees are sufficient for RAS.

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