

Infrared Spectroscopy in the Analysis, Characterization, and Testing of Coatings

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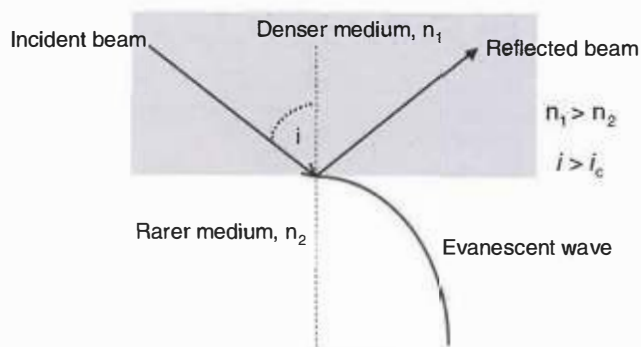
In this JCT COATINGS_{TECH} series of introductory tutorial articles, the emphasis sought is on the applications of modern analytical, characterization, and testing methods for coatings. And while it is easy to cite many examples of recent applications of mid-infrared spectroscopy, the most common sampling techniques employed have been well established for a long time and, as a consequence, mid-infrared spectroscopy has been at the forefront of analytical methods for characterizing coatings and surfaces for many years. In 1980, the Federation of Societies for Coatings Technology (FSCT) published an *Infrared Spectroscopy Atlas for the Coatings Industry*,¹ which contained over 1400 mid-infrared spectra, covering categories such as polymers, monomers, solvents, inorganic pigments and extenders, organic pigments, and various additives. A fourth edition of *Infrared Spectroscopy Atlas for the Coatings Industry*, which contains ca. 2500 mid-infrared spectra, was published in two volumes by the FSCT in 1991.² In addition to its established position as a favored technique for characterizing and analyzing polymers,³⁻⁶ the long tradition for using mid-infrared spectroscopy to study and characterize in situ coatings stems essentially from two sampling technique developments in the 1960s. The first, known as ATR (Attenuated Total Reflection) mid-infrared spectroscopy, is an internal reflection spectroscopy technique.⁷⁻¹¹ The second, more specialized technique is an external reflection approach undertaken at grazing angle of incidence, which is often referred to as RAIRS (Reflection-Absorption Infrared Spectroscopy),¹² or some other similar acronym. Mid-infrared ATR spec-

troscopy, which is discussed in more detail later, interrogates a surface layer of a sample to a depth in the approximate range of 0.3 μm to 3 μm . RAIRS is used to study thin films, typically in the range 100 $\text{\AA}$ – 100 nm, such as Langmuir-Blodgett and vacuum evaporated films and self-assembled monolayers supported on a smooth metal reflective surface such as that of gold, silver, and copper.¹³ RAIRS remains largely a more specialized research tool with one of its other main areas of application being in the study of species adsorbed on metal catalysts. However, since the 1980s, with the introduction of high sensitivity modern Fourier transform infrared spectrometers (FTIR), and in particular FTIR microscope systems, mid-infrared reflection-absorption spectroscopy at near normal angles of incidence has become quite a commonly used direct sampling technique for fingerprinting coating layers on reflective substrates. It is commonly referred to as the transflection sampling technique. Other mid-infrared sampling methods that have been used to examine coatings include transmission spectroscopy of material abraded from a surface, emission spectroscopy, and the more recently applied methods of photoacoustic and diffuse reflection

spectroscopy. Almeida et al.¹⁴ have discussed and compared the relative merits of a range of FTIR sampling techniques used for the study of surfaces and coatings. Sampling methods will be considered in more detail later.

The infrared portion of the electromagnetic spectrum is usually conveniently broken down into three separate regions. It is common practice today to label mid- and far-infrared bands with the unit of wavenumber, while near-infrared band positions are more usually quoted in units of wavelength. The mid-infrared region covers 4000 cm^{-1} to 400 cm^{-1} (2.5 μm to 25 μm wavelength); the near-infrared region extends over the range from ca. 750 nm to 2.5 μm ; and the far-infrared or lower wavenumber (longer wavelength) region occurs below 400 cm^{-1} .

Figure 1—Schematic of internal reflection spectroscopy. The infrared incident beam transmitted through the denser medium of refractive index n_1 is internally reflected at the boundary with the medium of lower refractive index n_2 , when incident at an angle of incidence i which is greater than the critical angle i_c .



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The strength of the mid-infrared region is that it is the range in which most of the fundamental vibrational frequencies of organic molecules occur. A mid-infrared absorption spectrum is generated when infrared radiation interacts in an appropriate manner with the molecular vibrations of a sample. Absorption bands that are characteristic of the organic molecular vibrations are seen throughout the spectrum of the sample, many occurring within relatively narrow wavenumber ranges that are associated with particular molecular groupings. For instance, hydrocarbon stretches (νCH) normally occur within the range $3200\text{--}2800\text{ cm}^{-1}$, with bands from vibrations of saturated species (e.g. $-\text{CH}_3$, $-\text{CH}_2$) occurring below 3000 cm^{-1} , while those associated with unsaturated groups, such as aromatic CH and $=\text{CH}_2$, usually occur above 3000 cm^{-1} ; the carbonyl ($\nu\text{C=O}$) will typically be found within the range $1850\text{--}1550\text{ cm}^{-1}$, with narrower regions within this range being more specific to type, such as ester, ketone, acid, etc.

Consequently, in addition to pattern-recognition fingerprinting of coatings, mid-infrared spectroscopy is also widely used as both a qualitative and quantitative tool for identifying or monitoring functional groups present on surfaces and in coatings, such as in a study of rate of cure or surface oxidation/degradation. Bands occurring in the near-infrared region are overtone and combination bands mostly of fundamental bands involving X-H (X = C, O, N) vibrations. Their relative intensity is one to several orders of magnitude less than those observed within the mid-infrared region, and a near-infrared spectrum tends to lack both the sensitivity and the fine detail necessary for it to be used as a general tool for characterizing coatings. It may, however, in some circumstances, provide a good method for gauging coat thickness/weight. The far-infrared region explores low-frequency motions in molecular systems (for example, skeletal bending modes of entire individual molecules) and has been more the realm of the academic researcher than of prime interest or value to industrial coatings technology. However, with the development recently of new Terahertz (THz) instrumentation there is renewed interest in this region, particularly within the pharmaceutical industry.¹⁵ In a recent publication, the potential for nondestructive analysis of tablet coating thickness was

demonstrated using THz pulsed imaging.¹⁶

Almost exclusively today, all mid-infrared spectrometers found in applications laboratories are Fourier transform spectrometers, because of their high sensitivity, excellent wavenumber reproducibility, and multiplex advantage.^{17,18}

MID-INFRARED SAMPLING TECHNIQUES

The ATR Technique

Internal reflection spectroscopy (IRS) is a consequence of the optical property that radiation passing through a denser (higher refractive index) medium at an angle of incidence greater than the critical angle will be totally internally reflected at a boundary in contact with a material of lower refractive index. A schematic of the ATR sampling method is shown in Figure 1. The evanescent wave is confined within the vicinity of the surface of the rarer medium.¹⁹ The

evanescent (exponentially decaying) wave decreases with intensity with distance normal to the surface into this rarer medium and can be envisaged as penetrating the surface layer of the rarer medium. The depth of penetration, d_p , has become a convenient comparative term for different experimental arrangements. It is actually the depth at which the amplitude of electric field amplitude falls to 37% (1/e) of its value at the surface. The depth of penetration depends on the angle of incidence and the ratio of the refractive indices of the denser to the rarer medium. It decreases with increasing angle of incidence. It is also wavelength dependent, increasing with increasing wavelength (decreasing wavenumber).

In the laboratory today, the most commonly used internal reflection elements are ZnSe, Type II diamond, and Ge. These have refractive indices (at ca. 1000 cm^{-1} and 25°) of 2.4, 2.4, and 4, respectively. Diamond, because of cost, is usually only configured for use in micro-ATR set-ups. Figure 2a compares d_p

Figure 2—(a) Plots of depth of penetration for two refractive indices (2.4 and 4) and two angles of incidence (45° and 60°). (b) Plots of effective sample path length using an internal reflection element of refractive index 4 at 45° angle of incidence for a single reflection element and $\times 3$, $\times 9$, and $\times 25$ multiple internal reflection elements.

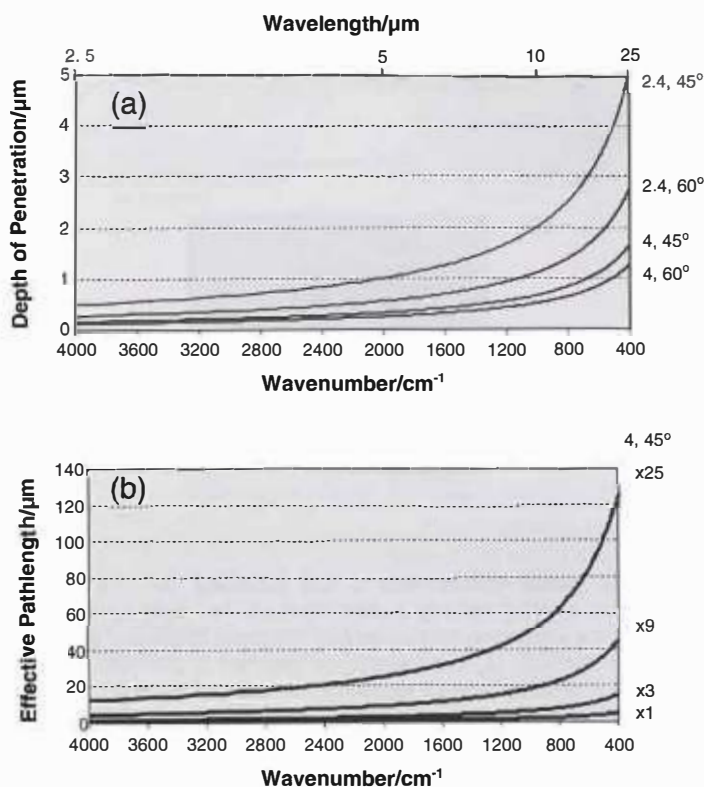


Figure 3—(a) Schematic showing multiple internal reflection. (b) Photograph of a horizontal multiple internal reflection accessory (Horizon™). Above the horizontal ATR element is a clamp for securing a solid sample into position onto the internal reflection element. A liquid sampling trough can be seen in the bottom left of the picture. (Photograph reproduced by permission of Harrick Scientific Corporation, Ossining, USA.)

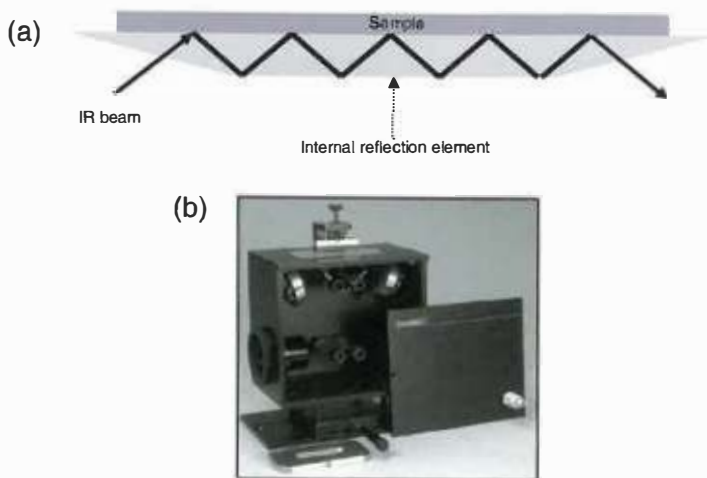
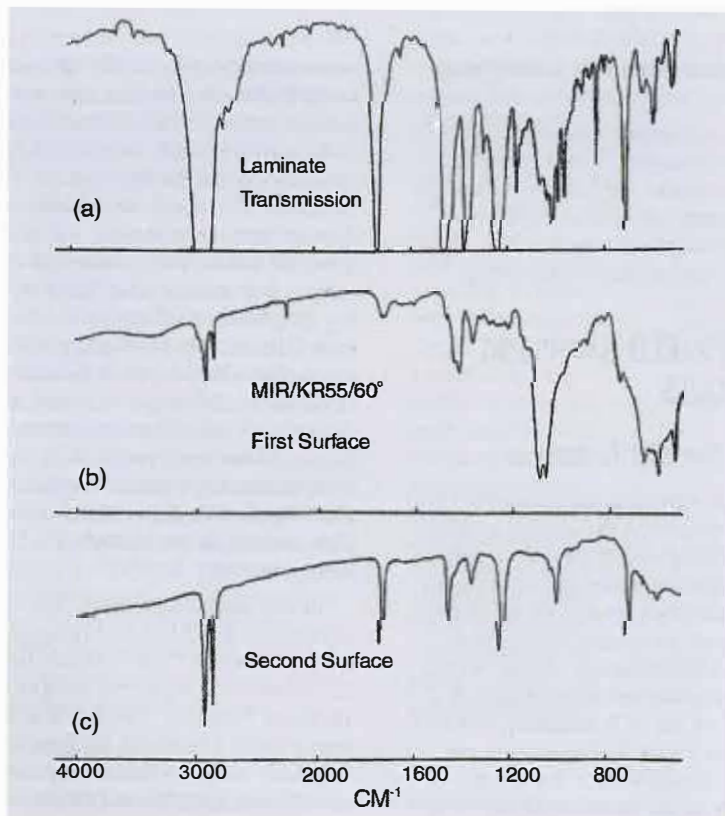


Figure 4—Mid-infrared spectra recorded from a food packaging film. The film comprises a polypropylene base with an ethylene/vinyl acetate copolymer heat-seal layer on one side (second, inner surface) and a vinylidene chloride/acrylonitrile/ester terpolymer barrier layer on the other side (first, outer surface). (a) is a transmission spectrum of the multilayer film; (b) and (c) are multiple internal reflection spectra recorded from each surface. In (b) and (c) characteristic spectra of each of the surface layers have been clearly isolated from that of the polypropylene base. In this measurement, a KRS-5 prism with a refractive index of ca. 2.4 at a 60° angle of incidence was employed. ©2000. Copyright John Wiley & Sons Ltd. (Reproduced with permission from reference 3.)



values calculated for a single internal reflection from both ZnSe and Ge internal reflection elements at two commonly used angles of incidence. It can be seen readily that the surface layer/coating thickness probed increases significantly towards lower wavenumber. A variety of geometrical shapes and sizes have been used for internal reflection elements, including tetrahedron, hemispherical, parallelepiped, trapezoid, and rod. One of the most commonly used in the laboratory now is the trapezoid, which is incorporated into the so-called horizontal ATR (H-ATR) units. These may be several centimeters long, allowing for multiple internal reflections, thus increasing the number of times the infrared radiation interacts with a sample surface (see Figures 2b and 3) and thereby increasing the effective sample layer pathlength. Although with the good signal-to-noise ratio spectra achieved routinely with a FTIR spectrometer, and because of their ease of use, modern single-reflection ATR accessories are being increasingly used to fingerprint coatings on polymer substrates. This is acceptable if the small contact region examined, typically of the order of 1 mm or less, may be considered representative of the coating layer. A classic example of the use of ATR spectroscopy is shown in Figure 4 in which the technique is used to identify the two different layers, one a heat-seal layer, the other a barrier layer, on each side of a food packaging film.³

RAIRS

Reflection Absorption Infrared Spectroscopy (RAIRS) at grazing angles of incidence, undertaken in practice typically at about 80° or greater, involves measurement of the change of reflectivity of a substrate brought about by a thin infrared absorbing layer.^{13,20} In addition to the absorption properties of the thin film, the absorption bands in a grazing incidence angle RAIRS measurement represent changes in reflectivity, $\Delta R/R$, which depend on the infrared standing wave intensity at the surface. Since changes in reflectivity $\Delta R/R$ due to the thin film are generally small (a few %), the experiment ideally needs to be carried out under conditions where R is substantial. Consequently, RAIRS is most successfully applied on metal surfaces, since the high reflectivity of the metal surface may be combined with an intense standing wave at the metal sur-

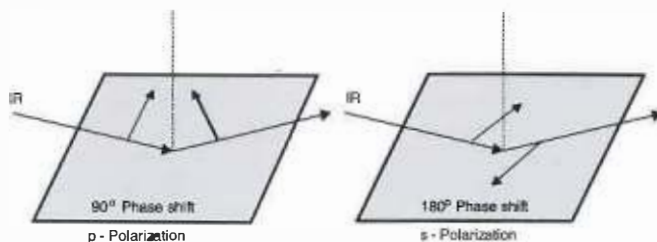
face. RAIRS is normally conducted using a polarizer set for p-polarized infrared radiation, because at a grazing angle of incidence for p-polarized radiation there is a phase change of about 90° . This results in the incident and reflected beams combining to produce a strong electric field which is effectively polarized perpendicular to the surface. For s-polarized radiation there is an 180° phase change on reflection and as a consequence a node in the electric field occurs at the metal surface. These properties lead to the metal surface selection rule, which states that only vibrational modes with dipole moment components perpendicular to the metal surface may be excited, and allow one to evaluate molecular orientation in ultra-thin films, such as self-assembled monolayers. Figure 5 is a schematic showing the sum of the incident and reflected vectors for s- and p-polarization.

Tolstoy et al.²¹ have recently published a handbook that covers in detail and reviews the theory, for both flat and powdered substrates, the practical methods of measurement and applications of mid-infrared spectra recorded from ultrathin films (films of ~ 1 nm thickness) covering submonolayer to several monolayers. Depending on the system, infrared spectroscopy may be sensitive to 10^{-5} – 10% of a monolayer.²¹ These nanotechnology films, which find applications in microelectronics and optoelectronics, may be used, for example, as passivating or protective coatings.

Photoacoustic Spectroscopy

Photoacoustic spectroscopy (PAS), as a mid-infrared laboratory sampling technique, came to prominence shortly after the advent of modern FTIR spectroscopy. The approach offered some unique advantages. It is less sensitive to surface condition than ATR and can be used to probe a greater range of sampling depths, from several to 100 mm or greater.^{20,22} In a photoacoustic FTIR measurement, the mid-infrared beam is incident on the sample, which is placed inside a cell filled with a coupling gas, usually He. The modulated FTIR beam that is absorbed by the sample causes absorption-induced heating in the sample and consequent oscillations of the sample temperature. The thermal waves propagate to the sample surface, producing pressure fluctuations in the coupling gas. The absorption characteristics of the sample are measured by sensing

Figure 5—Schematics of grazing-incidence reflection-absorption spectroscopy showing how for p-polarization the electric field vectors near the sample surface sum, while for s-polarization they effectively cancel.



with a microphone the thermal-expansion pressurization of the coupling gas caused by heat transfer. The magnitude of a PAS signal varies linearly with increasing absorbance, which can be a consequence of either concentration or sampling depth or both. However, the dependence is nonlinear at extremes of low and high values of absorptivity, and signal saturation occurs at high signal levels. The phase of the PAS signal, which corresponds to the time delay associated with heat transfer in the sample, may be used to determine the depth within the sample from which the PAS signal originated.

In a conventional rapid scan FTIR spectrometer, lowering the scan speed (mirror velocity), thus decreasing the frequency of modulation of the mid-infrared beam, will increase the sampling depth. However, the modulation frequency in this scanning mode is wavelength dependent and increases with increasing wavelength, so like ATR spectra when compared with transmission spectra, the relative intensities of bands in a PAS spectrum appear more enhanced with decreasing wavenumber. Figure 6 shows a series of FTIR PA spectra recorded using different interferometer mirror scan speeds from a polytetrafluoroethylene (PTFE)/polyimide layered structure. While at the fastest scan speed the PA

spectrum is almost entirely due to the uppermost PTFE layer, at decreasing interferometer mirror scan speeds there is increasing intrusion into the PTFE spectrum of bands characteristic of the underlying polyimide layer.

The variation in modulation frequency can be overcome by using a step-scan interferometer, whereby an external

Figure 6—Mid-infrared rapid scan FTIR spectra from a PTFE/polyimide/PTFE layered sample, with layer thickness of 12.5 μm , 50 μm , and 12.5 μm , respectively, recorded at different interferometer mirror scan speeds. Note how there is increasing contribution to the recorded spectrum from bands characteristic of the polyimide with decreasing mirror scan speed, i.e. decreasing modulation frequency.

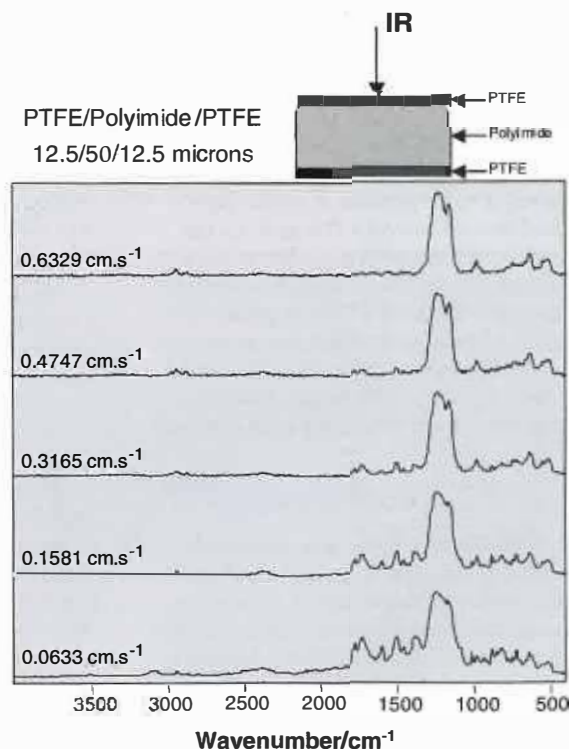
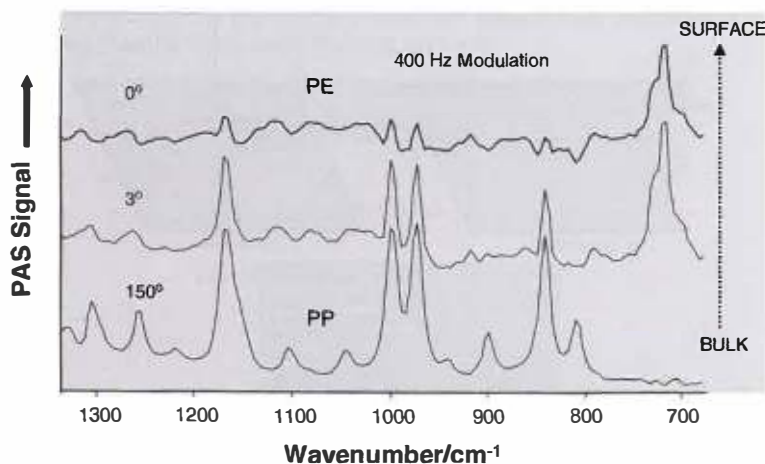


Figure 7—Phase-rotated spectra extracted from a 400 Hz phase modulation PAS FTIR step-scan measurement on a 25- μm thickness commercial polypropylene film.²³



modulation is applied such that each wavenumber within a spectrum is subjected to the same modulation frequency, thereby enabling mid-infrared spectra to be derived from particular depths—a process that may be envisaged as “optical sectioning.” A simple example is shown in Figure 7, which shows the phase-rotated spectra derived from a 400 Hz phase-modulated step-scan FTIR measurement from a 25 μm -thick commercial film based on polypropylene.²³ The PAS spectra shown correspond to those extracted at 0°, 30°, and 150° phase rotation. The bulk (150°) spectrum is clearly that of polypropylene homopolymer. While of lower signal-to-noise ratio, the surface (0°) spectrum clearly indicates that the coating layer is polyethylene. This was thought to be present at a coat layer thickness of between 0.4 and 0.5 μm . In this case we were not able to obtain such good discrimination by multiple internal reflection ATR (Ge prism, 45° angle of incidence) spectroscopy, since in the fingerprint region of the mid-infrared spectrum the nominal depth of penetration was calculated at ca. 0.95 μm .

Transflection

Transflection is the term used to describe a near-normal incidence reflection-absorption measurement. It derives from measuring a coating on a reflective substrate, in which the mid-infrared beam at a near-normal angle of incidence (typically ca. 0°–30°) passes through the coating, is reflected back from the

substrate, and passes through the coating again before being detected. The resulting double-pass spectrum will therefore resemble that recorded in transmission from a sample of about twice the coating thickness. However, superimposed on this reflection-absorption spectrum will be a specular (front-surface) reflection spectrum. This specular reflection spectrum exhibits the dispersion in the refractive index that occurs through an infrared absorption band. It leads to apparent distortion of the infrared absorption spectrum, particularly noticeable for strong bands, and its influence clearly increases with decreasing coating thickness. In evaluating FTIR transreflectance spectra, it is important that the influence of the specular reflectance component is appreciated, otherwise erroneous results and correlations may likely be formed.¹⁸

The sampling technique can provide a very quick and convenient way of fingerprinting coatings on applications such as the insides of beverage cans.

FTIR Microscopy

Transflection is one of a range of sampling techniques, along with transmission and micro-ATR spectroscopy, that are commonly used with FTIR microscopy. The coupling of microscopy with FTIR spectroscopy has enabled the study and measurement at high lateral spatial resolution of a wide range of samples and problems related to the coatings industry. It is widely used in

industry, alongside a range of other analytical techniques, in a forensic capacity for elucidating problems associated with surface/coating defects/imperfections, contamination, and failure. Typically these examinations are limited to a localized area of greater than ca. 10 μm diameter, although using the mid-infrared radiation emanating from a synchrotron does offer significant advantages at high lateral spatial resolution.²⁴

For characterizing thick coating/surface layers (ca. ≥ 10 mm thickness), it is often relatively straightforward to microtome a cross-section from a multi-layer structure and interrogate the coating and other layers independently by a transmission measurement.

In addition, to single-point spectra, FTIR ATR-microscopy coupled with using a Focal Plane Array (FPA) detector offers the potential to image surface heterogeneity and composition.²⁰ Different species and phases of the order of the pixel size of the array, which is usually about 6.25 $\mu\text{m} \times 6.25 \mu\text{m}$, may be highlighted; a typical array detector today may comprise 64 $\times$ 64 or 128 $\times$ 128 pixels.

Other Sampling Techniques

As appropriate, a range of other mid-infrared sampling techniques have been applied to studies and problems relating to the coatings industry, although in recent years not as widely as those considered above. These include: transmission, emission, and diffuse reflection. Historically, abrasion was often employed, whereby surface material was abraded and examined in transmission as a KBr disc.²⁵ Abraded material may now be more conveniently examined by diffuse reflection, where the abraded material is simply dispersed in and analyzed as a mixture with dry, powdered KCl.¹⁸ Collecting diffuse reflection spectra from surfaces that are overlaid with dry powdered KCl has also been employed in particular circumstances, such as that of recording mid-infrared spectra from coupling agents coated onto silica glass fibers.²⁶ Since a sample that absorbs mid-infrared radiation will also emit mid-infrared radiation, an analytically useful emission spectrum may also be recorded from a thin coating layer on a metallic substrate by emission spectroscopy.²⁷ In the laboratory, emission spectroscopy has been supplanted largely as a sampling technique for fingerprint-

ing thin coatings on reflective metal substrates by the more convenient transfection approach.

APPLICATIONS AND EXAMPLES

Since this article is not intended as a review, but as a fairly concise tutorial, the references included have been chosen simply to illustrate a particular type of application. Many are from more recent published work; they are, however, very far from being exhaustive and fully representative of the wide range of analyses undertaken and materials studied. For the majority of practical purposes, the intensity of a mid-infrared absorption band is proportional to the number density of vibrating species giving rise to that band. Hence, monitoring of the relative intensity of a mid-infrared functional group band or the ratio of two bands can be an extremely useful method, and is widely used in the study of coating cure processes and coating and surface layer weathering and degradation. In addition to being very characteristic of the functional groups present and their concentration, mid-infrared spectra of organic polymers may also be very sensitive to state of order. They are characteristic also of stereoregularity, molecular conformation, and molecular orientation and ordering.^{54,20}

Coating Identification, Chemical Structure, and Thickness Determination

A straightforward coatings application of mid-infrared ATR spectroscopy is illustrated in Figure 4 and represents probably one of the more common uses of mid-infrared spectroscopy in industry—that of fingerprinting organic polymer coatings on multilayer samples that are thicker than about 1 μm . For coatings that are thinner than this and on an organic polymer substrate, there will be intrusion of absorption bands of the substrate within the recorded ATR spectrum. However, while a "pure" spectrum of the coating may not necessarily be isolated in this manner, if a suitable window is available within the substrate's mid-infrared spectrum in which an absorption band of the coating is present, a coating layer thickness may be determined to a much lower thickness value. Providing a method can be

calibrated by reference to values determined by some other suitable means, then precise quantitative practical methods suitable for at-line monitoring of a coating thickness may be developed. In my time in the plastics industry, we developed mid-infrared ATR-spectroscopy quality assurance methods that were applied routinely for determining coat thickness (or coat weight) levels down to the order of 500 Å or less.

Curing and Film Formation Studies

The particular sensitivity of mid-infrared spectroscopy to oxygenated species, such as hydroxyl and carbonyl groups, and unsaturated species, such as many double and triple bonds, makes it a particularly valuable analytical technique and investigative tool for the coatings industry.

There are many published studies using mid-infrared spectroscopy that relate to polymer cure and crosslinking mechanisms and rate; many are cited within references 3–5. Kinetic studies undertaken with a modern rapid scan FTIR spectrometer allow for sequential spectra to be recorded at time-intervals much lower than 1 sec if necessary. Many studies of thermal cure and UV-curable mechanisms are made in transmission or using internal reflection spectroscopy from thin films cast from resin solutions or in situ onto a polymer base film or metallic substrate.

Typical of these are thermal cure of epoxy resin based coating systems, for which the rate of cure may be followed simply by observing the reduction in absorption intensity of a band at 915 cm^{-1} attributed to the epoxy ring. Another common example is that of following the cure reaction of a polyurethane lacquer by monitoring the decrease of a band due to the isocyanate group. Dual-cure

formulations have been developed to overcome cure deficiencies in UV non-illuminated areas of protective coatings, such as those in shadowed areas of three-dimensional structures or deep within thick, pigmented coatings. In a recent study, Stader et al.²⁸ monitored in real-time the decay in intensity of the characteristic isocyanate band occurring at 2271 cm^{-1} in a thermal and photochemical curing study of a "dual-cure" system, in which the depletion of the acrylate bonds was monitored at 1410 cm^{-1} . The spectra shown in Figure 8 are taken from a real-time mid-infrared spectroscopic monitoring of a UV-curable resin.²⁹ In this instance, the reflection-absorption spectra were recorded using a rapid scan FTIR spectrometer from a resin sample on an Al substrate contained within a heatable reflection-absorption cell. The UV illumination was switched on and off with a high-speed shutter synchronized with the scan system of the FTIR spectrometer. In Figure 8 the series of spectra were recorded at 45 min time intervals during the photoinduced polymerization reaction. They represent the difference between the recorded spectrum and that of the uncured resin. The negative doublet at 1615 cm^{-1} and 1636 cm^{-1} results from a decrease in the acrylic C=C concentration; the negative C-O peak at 1680 cm^{-1} results from a decrease in the photoinitiator concentration; the peaks at 1725 cm^{-1} and 1740 cm^{-1} are a consequence of frequency shifts of the acrylic C=O band arising from a loss of conju-

Figure 8—Series of mid-infrared difference spectra derived from spectra recorded at 45 min time intervals during the UV-curing reaction of an acrylate resin. (Reproduced from reference 29, ©2000, with permission from Elsevier.)

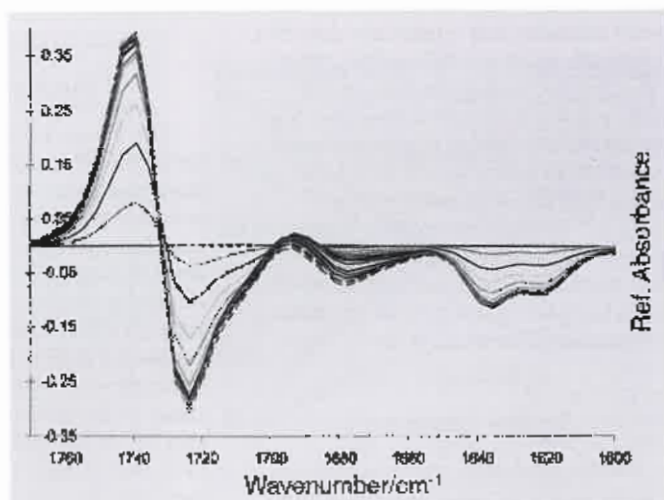
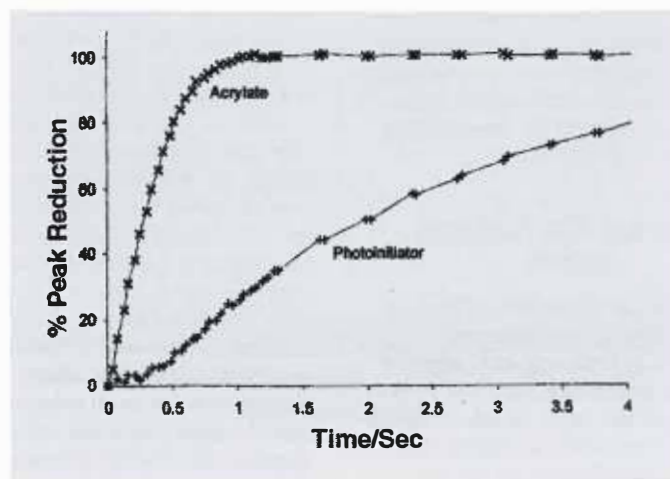


Figure 9—UV-curing profiles of lauryl acrylate with 10% photoinitiator. The relative decrease of the acrylate was determined from the intensity of a mid-infrared peak at 810 cm^{-1} ; the photoinitiator relative concentration decrease was determined from the carbonyl band at 1680 cm^{-1} . (Reproduced from reference 29, ©2000, with permission from Elsevier.)



gation. Figure 9 compares the UV-curing profile determined from a reflection-absorption study under nitrogen of a $5\text{-}\mu\text{m}$ thick film of lauryl acrylate containing a high concentration (10%) of the photoinitiator Irgacure 184 with the decrease in intensity of the carbonyl band due to the photoinitiator.²⁹ A band at 810 cm^{-1} , attributed to the acrylate $\text{C}=\text{C}-\text{H}$ group, was used to monitor the consumption of $\text{C}=\text{C}$ groups in terms of a percentage reduction in intensity. A carbonyl band at 1680 cm^{-1} was used to monitor the decrease in photoinitiator. The rapid scan FTIR system is clearly well-capable of following the UV-curing process, and shows that in the first 0.5 sec of UV illumination that ca. 70% conversion has taken place and that conversion of the $\text{C}=\text{C}$ is completed after ca. 1.2 sec.²⁹ The kinetics of the carbonyl intensity loss apparently does not mirror the resin curing reaction. After initiating the curing reaction, in a secondary reaction the photoinitiator concentration is depleted in a bimolecular reduction step that results in a decrease in the number of initiator carbonyl groups.²⁹ Thermal curing of a polyimide prepolymer and cyclization to imide formation may also be observed readily by an increase in intensity of an imide carbonyl band near 1780 cm^{-1} .

Surface Treatments

Surface oxidation, corona discharge, plasma treatment, and solvent etching

have all been employed to enhance adhesion of polymer surfaces and each imparts a modification to the surface, either chemically by introducing specific functional groups, such as $-\text{OH}$, $-\text{NH}$, $\text{C}=\text{O}$, $-\text{ONO}_2$, or fluorination, or by a change in surface crystallinity.^{5,25} These surface property modifications are often observable readily in a mid-infrared ATR spectrum recorded from the modified surface layer. In a recently reported study,³⁰ FTIR spectroscopy was used to complement X-ray photoemission spectroscopy (XPS) to characterize acrylic acid thin films deposited by RF plasma assisted chemical vapor deposition, as part of an investigation into surface engineering of polymeric film coatings and its influence on protein attachment kinetics for biomedical applications.

Durability Studies

There have been many reported studies of the effects of weathering, degradation, and oxidation on a wide variety of polymer surfaces. For instance, Johnson and McIntyre³¹ reviewed the potential of several analytical test methods for UV durability predictions of polymer coatings. Of those evaluated, electron spin resonance (ESR) and FTIR-ATR spectroscopy were deduced as preferable because of the short exposure times necessary to obtain significant results under UVA that predict, quantitatively, a coating's lifetime. Decker et al.^{32,33} used

mid-infrared FTIR spectroscopy recently to study the drying and UV-radiation curing³² and weathering resistance³³ of water-based UV-cured polyurethane-acrylate (PUA) coatings. Initially in the weathering resistance study, after drying, the UV-curing reaction was monitored by real-time mid-infrared spectroscopy by following the decrease in intensity of a band associated with the acrylate double bond. The extent of photodegradation to UV exposure was then evaluated by observing relative intensity changes in characteristic bands. For instance, Figure 10a compares the mid-infrared spectra of a UV-cured water-based PUA coating before and after 2000 hr accelerated UVA-weathering, while Figure 10b shows an example of the decay of CH and urethane linkages and build-up of oxidative products from a PUA coating with variation in exposure time. Yang et al.³⁴ used both mid-infrared step-scan PAS and ATR-microscopy in an accelerated weathering (QUV) degradation study of a high gloss polyurethane topcoat over a chromate pigmented epoxy primer. Their observations supported increased formation of polyurea at the film-air interface with increasing exposure time. Keene et al.^{35,36} have very recently published FTIR microscopy and topographical detailed investigations into failure analysis of Navy coating systems. A diamond-element micro-ATR system was used to collect spectra from the sample surfaces. In addition, cross-sections of the two different high-solids poly(ester-urethane) military coating systems from different aging protocols were microtomed to a thickness of $3\text{ }\mu\text{m}$, and examined by transmission FTIR microscopy with a sampling aperture of $10\text{ }\mu\text{m} \times 70\text{ }\mu\text{m}$.³⁵ The depth-resolved examinations allowed for a vertical sampling resolution within the topcoat of approximately $5\text{--}10\text{ }\mu\text{m}$.

A wide variety of mid-infrared spectroscopic photodegradation studies of paint films have been reported, and many are cited in a recent review article of vibrational spectroscopy in the paint industry.³⁷ In one of the reported studies, micro-ATR was used to evaluate and compare the degradation of coatings after one-year exposure in Florida. While, for a white water-based acrylic system the observed changes in its mid-infrared spectrum were small, being confined essentially to an increase in hydroxyl groups (3430 cm^{-1}), a shift in the carbonyl band, and possibly an increased intensity between 1650 and 1600 cm^{-1} ,

a white water-based alkyd paint showed much greater changes throughout its spectrum. Reference 37 also contains a table listing changes observed in the mid-infrared spectra on degradation of a range of binder materials.

Stratification and Migration

For mixed systems such as paints, it can be important not just to characterize a bulk layer, but to also to investigate whether any stratification of the components has occurred, either by design or failure. For very thick films, clearly cross-sectioning and measuring successive layer thickness elements by transmission mid-infrared microspectroscopy is a possibility. For thin films, both step-scan PAS and ATR may be used for depth profiling. A simple example from reference 37 of a self-stratifying coating system is shown in Figure 11. The paint was cast onto a metal foil. An ATR spectrum was recorded directly from the film's top surface, showing it to be almost entirely composed of a fluorinated resin; the spectrum of the other surface was obtained by directly casting the paint onto an ATR internal reflection element. This surface was predominantly that of the epoxy resin.

Since enrichment of a surfactant at an interface may adversely affect a paint's properties, such as water sensitivity or adhesion, it is important to be able to depth profile the composition of a coating layer.³⁷ While using different angles of incidence and different re-

fractive index ATR elements allows for some mid-infrared spectroscopy depth profiling, its range is limited and it is infrared wavelength dependent. A greater depth range is achievable with step-scan PAS and the depth probed is independent of the radiation wavelength. Both ATR and step-scan PAS have been employed in analyzing possible migration of surfactants, which are present in most latex and emulsion paints.³⁷ As an example, both techniques have been used in a detailed quantitative study of films formed from mixtures of polystyrene and poly(*n*-butyl acrylate) latexes with the anionic surfactant sodium dioctyl sulfosuccinate (SDOSS).³⁸ The location of nonassociated surfactant can be ascertained from a characteristic SO_3^- group absorption band at 1050 cm^{-1} arising from free $\text{SO}_3^- \text{Na}^+$ on the SDOSS; bands due to associated SDOSS occur at 1046 cm^{-1} and 1056 cm^{-1} for water association and acid association, respectively. The ATR measurements were undertaken using polarized mid-infrared radiation to gain insight into the orientation of SDOSS molecules, particularly near interfaces, while step-scan PAS was used to probe depths up to $22\text{ }\mu\text{m}$ from either the film-air or the film-substrate interface. Some observations that were deduced from the data were: that surfactant molecules accumulate near both interfacial regions; that there is a high concentration of surfactant groups near the film-air interface; and that at shallow depths the nonassociated

SDOSS groups are aligned preferentially perpendicular to this surface, while the associated groups are oriented with a parallel preference. (Full details of the experimental procedure and results diagnosis may be found in reference 38; other migration studies may be found in references 37 and 38 and references therein.)

Other Applications

The published literature on the use of mid-infrared spectroscopy to identify, characterize, and elucidate on a coating's performance is extensive and in the space available here to discuss its contribution to the coating's industry the number of application examples and fields has had to be very limited. There are many specialized and diverse areas such as surface engineering, inorganics, paper coating, electronic devices, and biocompatibility where mid-infrared spectra can give insight and understanding into a coating product's performance. For instance, conducting polymers have been shown to have excellent corrosion resistance,³⁹ and in a study of the corrosion protection properties of a polyaniline-polypyrrole composite coating on Al panels, reflection-absorption infrared spectroscopy was used to compare the chemical structure of the various inorganic-filled formulations of coatings that were produced by electrochemical polymerization. Manso et al.⁴⁰ used FTIR (alongside XRD and SEM-EDX) in

Figure 10—(a) Mid-infrared spectra of a UV-cured water-based PUA coating before (continuous line) and after (dashed line) 2000 hr QUV-A weathering. (b) Plots derived from mid-infrared data showing the decay of CH and urethane linkages and build-up of oxidative products from a QUV aging of a PUA coating with variation in exposure time. (Reproduced from reference 33, ©2004, with permission from Elsevier.)

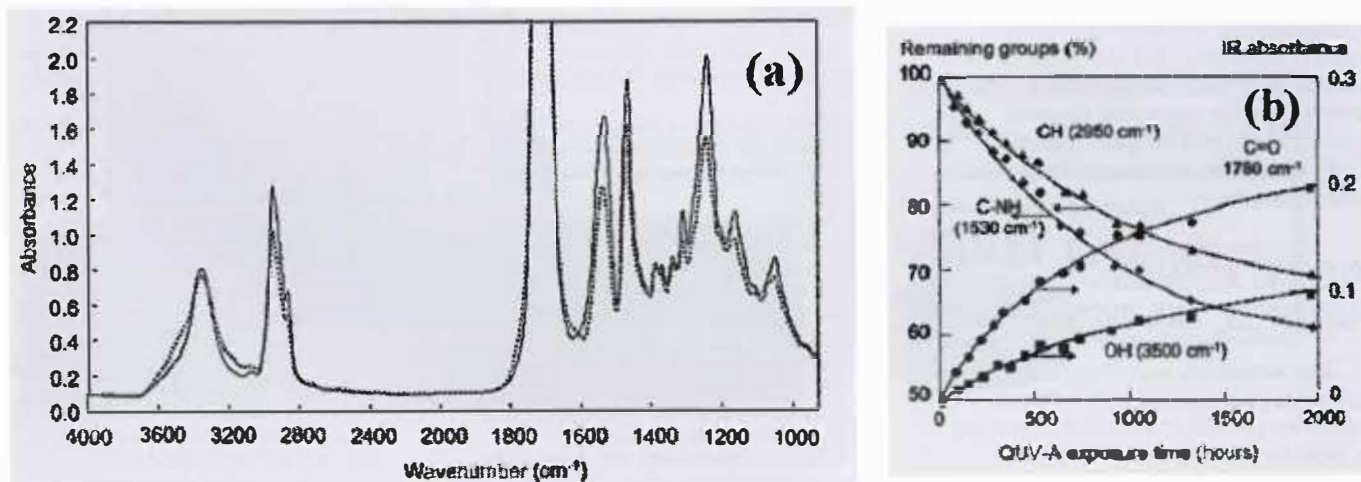
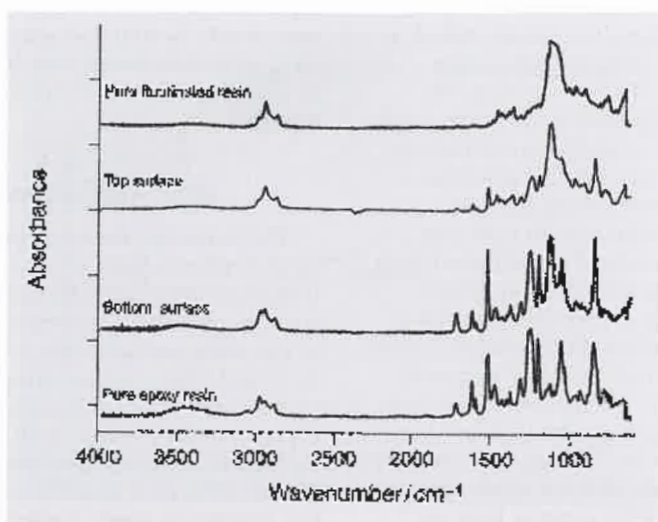


Figure 11—Mid-infrared spectra recorded from the surfaces of a self-stratifying epoxy resin-fluorinated resin coating system. Also shown are reference spectra of the pure resins. (≈ 2002 , Copyright John Wiley & Sons Ltd. Reproduced with permission from reference 37.)



testing sol-gel CaTiO_3 coatings for bio-compatible applications.

The applications emphasized in this article have been towards those investigations that are undertaken typically within a research, technical, or production support laboratory. The sensitivity of mid-infrared spectroscopy to functional group type and concentration clearly makes it also a favored method for simple monitoring of a product synthesis, both in the laboratory and at-line, and for on-line measurements during product manufacture. Near-infrared gauges for cross-web scanning of films for monitoring web-based coat-weight and determining moisture levels during product manufacture are also widely used.⁴¹ Both mid- and near-infrared spectroscopy also find uses in compositional monitoring, product quality assurance, and raw material validation. Mid infrared spectroscopy may also be used to sense and quantify vented vapor and off-gas emissions, both within the working environment and remotely.

CLOSING REMARKS, ADVANCES, AND PROSPECT

The sensitivity, specificity, and diversity of applications of mid-infrared spectroscopy will ensure that it remains a popular and prominent analytical

technique within the coatings industry. Undoubtedly, there will be increased use of both near- and mid-infrared technology in process analytical measurements, and one has yet to see the potential of imaging applied to problems of coating uniformity and heterogeneity. Also, novel techniques, such as mid-infrared photothermal microspectroscopy (PTMS), are being developed and evaluated.⁴² PTMS, when combined with other scanning probe microscopy techniques, should allow for the nondestructive localized mapping of the topology and chemical and thermal characteristics of a coating at high lateral spatial resolution. $\square$

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