FMIR Infrared Spectroscopy of Coatings on Fibers and Metal Plates*

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Synopsis

The FMIR technique offers a new and improved means of identifying coatings on fibers, elucidating coating–substrate bonds, and determining the nature of absorption sites on substrates by infrared spectroscopy. This technique is based on the internal reflectance of radiation in the middle infrared region. The ability to obtain infrared spectra of surface materials without removing the materials from the fiber gives the FMIR technique a noteworthy advantage over transmission techniques.

The present work was undertaken to develop a direct method of identifying coatings on fibers, to elucidate coating–substrate bonds, and to determine the nature of absorption sites of glass fibers. Serious problems were encountered with infrared transmission techniques: (1) conventional techniques which required preliminary separation and concentration steps caused loss and contamination of samples and loss of time; (2) solvents and mulling materials masked important portions of spectra; and (3) the physical and chemical properties of both the coating and substrate were slightly modified by removing the coating from the substrate.

Attenuated total reflectance (ATR) spectroscopy† in the infrared region makes possible the rapid and direct analysis of fibrous materials.[1] Generally, the spectral bands produced by ATR are distorted, and at times, bands produced by conventional transmission techniques do not appear in ATR spectra. These differences are a severe deterrent to the spectroscopist when group correlations for an unknown coating are required. Also, the single-reflection technique is unsuited for a study of coatings on fibers because infrared radiation is transmitted through only a small area of sample. Most of these problems are solved by increasing the number of reflections.

In frustrated multiple internal reflectance (FMIR) spectroscopy, many reflections occur at the sample–plate interface; thus, absorbances are amplified at each reflection. Two advantages are thus gained over the single-reflection approach: the spectra of films a few molecular layers thick

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† ATR is considered a single reflection technique by the author; the many- or multi-ATR technique is considered the same as the frustrated multiple internal reflectance technique.

FREQUENCY (CM⁻¹)
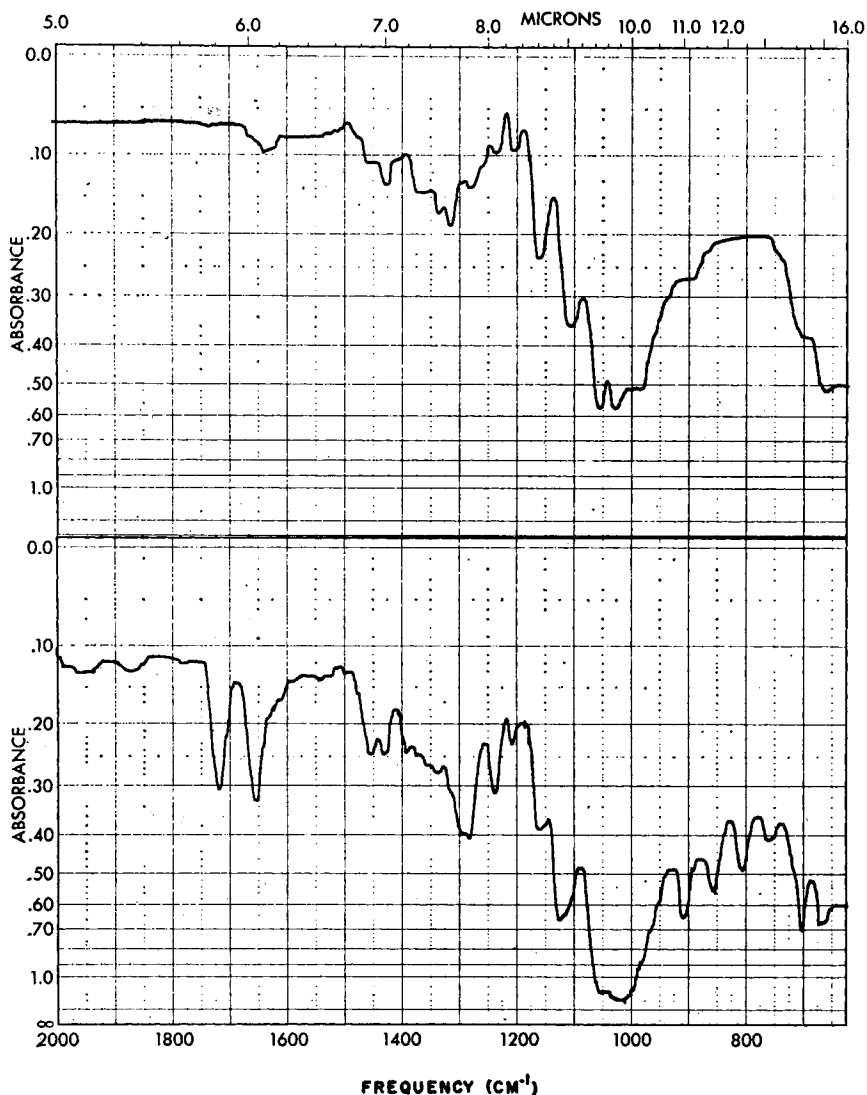
(a) top   (b) bottom

Figure 1. See caption p. 3955.

can be measured, and the resulting spectra resemble more closely spectra obtained by conventional transmission techniques.[2] In this approach, infrared energy is focused on the end of an infrared-transmitting plate in such a manner that the incident beam is totally reflected internally several hundred times. The electric field of the reflected waves penetrates many times into the sample which is placed on the surface of the plate. The field is frustrated by the material at characteristic frequencies, and a plot of the unfrustrated (transmitted) radiation versus frequency (cm.⁻¹) gives a curve
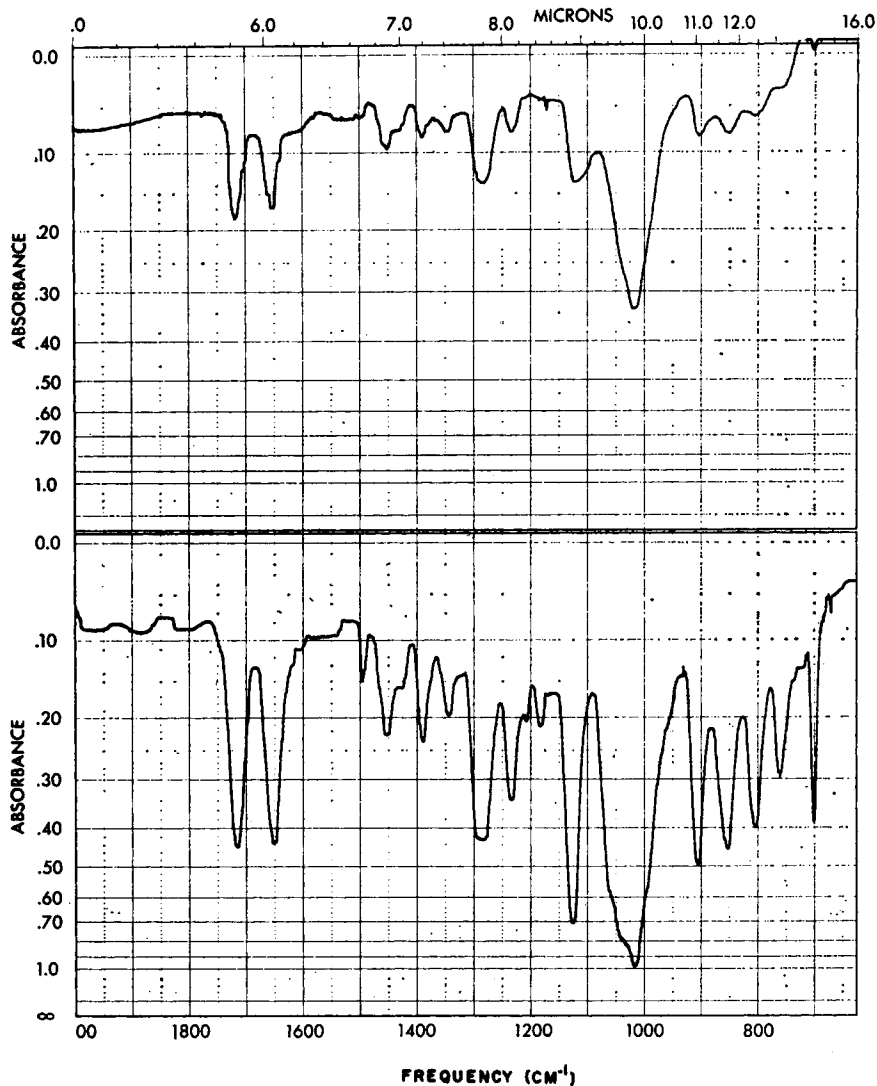
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Fig. 1. (a) FMIR spectrum of cotton fibers;   (b) FMIR spectrum of cotton fibers coated with a phenylcarbethoxyvinyl compound;   (c) differential spectrum of the coating; (d) FMIR spectrum of the coating.

nearly identical with a conventional transmission spectrum.   All bands in ordinary transmission spectra are present in FMIR spectra and have approximately the same shapes and relative intensities.[3]   Consequently, unknown materials can be identified by comparing their FMIR spectra with collections of standard transmission spectra.   More important, compounds can be identified, with minor corrections for slight band displacements and dispersion in the vicinity of the absorption bands, by group-

correlation techniques. Thus, the attributes of FMIR make the technique suitable for the direct study of surface phenomena.

Experimental

The FMIR spectra in this study were obtained on samples of coated and uncoated fibers prepared by forming them into pads, ca. 50 × 20 mm., and on samples of steel plates cut to the same size. The samples were held between two KRS-5 plates (50 × 20 × 0.2 mm.) by means of a metal vise. The entire assembly was placed in a Wilks Model 8B internal reflection spectrophotometer, and the samples were scanned in the region 4000–625 cm.$^{-1}$

Results and Discussion

The spectrum of cotton fibers in the region 2000–625 cm.$^{-1}$ is presented in Figure 1a. Strong absorption bands are produced by the cellulose in the range 1150–900 cm.$^{-1}$ The spectrum of the same cotton fibers, coated with a phenylcarbethoxyvinyl compound, is presented in Figure 1b. A differential spectrum of the coating is presented in Figure 1c. The differential spectrum was obtained by mounting a pad of uncoated cotton against a KRS-5 plate in the reference beam and the pad of coated cotton in the sample beam. The spectrum of the coating itself is presented in Figure 1d.

When uncoated cellulose fibers are simply placed against the reference place to cancel strongly absorbing cellulose bands, the response of the instrument is usually poor. In Figure 1c the cellulose bands have been cancelled, but the bands produced by the coating in the region 1200–900 cm.$^{-1}$ are poorly defined, and only tentative spectral assignments can be made in this region. Consequently, spectra outside this region must usually be obtained for cellulose and other plant fibers. However, this interference is not a problem when the fiber possesses only bands of medium or weak strength. These bands can easily be cancelled out of the spectrum of coatings if the uncoated fiber is placed against the reference plate and the intensity of the absorption is controlled by adjusting the size of sample or the sample-to-plate pressure. The latter technique is much more convenient because the pressure is readily adjusted by set-screws on the vise. Sufficient energy is transmitted through the plates when cancelling medium or weak bands so that the response of the instrument remains essentially unchanged.

The FMIR technique has been employed to study the mechanism of electrodeposition of organic polymers from aqueous suspensions onto mild steel plates. The spectrum of a modified linseed oil-type polymer coated on an internal reflection plate is presented in Figure 2a. Strong absorption bands are produced by this polymer in the range 2000–625 cm.$^{-1}$ The spectrum of the same polymer, 1 μ thick, electrodeposited on a mild steel plate, is presented in Figure 2b. The voltage is 140 v., and the time of electrodeposition is 3 sec. The spectrum of the same polymer, 0.5 μ thick,

electrodeposited on another mild steel plate is presented in Figure 2c. The voltage and time of electrodeposition are 100 v. and 2 sec., respectively. The spectrum of still another coated mild steel plate immersed in the same suspension for 2 sec. at 30 v. is presented in Figure 2d. The thickness of the coating on the last plate is less than 0.1 μ. These experiments demonstrate that a polymer coated onto a hard surface can readily be identified. In addition, these experiments suggest that low molecular weight acids which apparently produce the spectrum in Figure 2d are electrodeposited onto the mild steel immediately before the polymer electrodeposits.

The studies of glass fibers were mainly concerned with interactions that occur at the coating-fiber interface. The glass fibers were composed of aluminoborosilicate, composition E. These fibers had a clean, untreated surface; i.e., the attenuated fibers were passed through distilled water rather than chemicals. The physically sorbed water was removed by heating *in vacuo*. The fibers were placed in a vacuum-distillation apparatus and exposed to pyridine for 1 hr. at 150°C. at a few millimeters pressure; then the distillation apparatus was evacuated to remove all nonsorbed pyridine. The coated fibers were placed against a KRS-5 plate and a FMIR-infrared spectrum was obtained. Five very weak infrared absorption bands produced by the pyridine molecules were observed at 2890, 1610, 1540, 1500, and 1440 cm.$^{-1}$ This experiment confirmed the sorption of pyridine on the glass fibers and also tentatively indicated the nature of adsorption sites on the glass substrate by the position of the pyridine ring modes near 1540, 1500, and 1440 cm.$^{-1}$ The position of the bands for pyridine on silica-alumina catalysts[4] are similar to those observed in this study. These bands indicate that pyridine is chemisorbed at both Lewis and Brönsted sites on the glass surface.
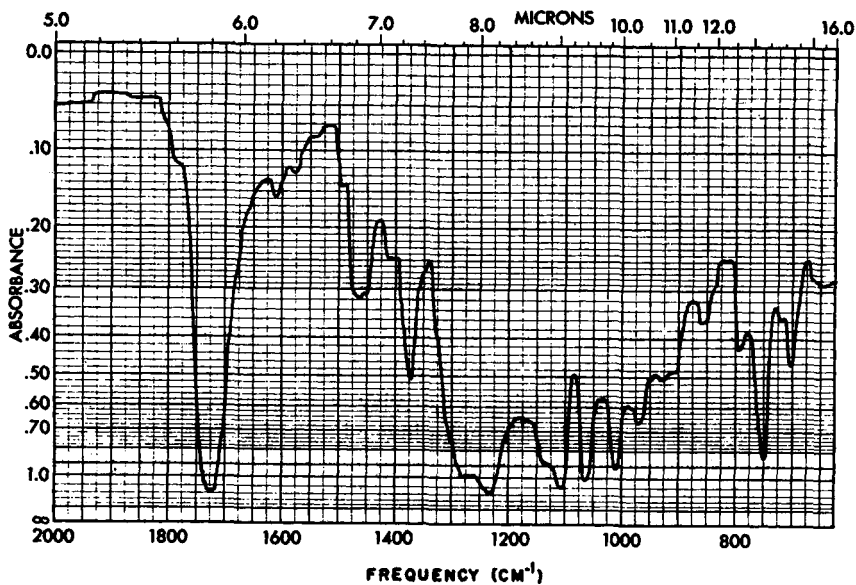
Sensitivity

The high sensitivity of the FMIR technique has made possible the analysis of small amounts of material coated on relatively small areas. One of the major factors influencing sensitivity is, of course, the molar absorptivity of the absorption band. The lower limit of sensitivity for coatings composed of groups that yield very strong infrared absorption bands such as carbonyl, is about 0.5–1% (area/area) of material on the surface of the fiber; for weaker bands such as C–C stretching modes, the lower limit of sensitivity is about 10–15% (area/area) of material on the fiber surface. These levels were calculated on the assumption that an identifiable band should have at least 0.05% absorbance.

Another factor which increases the sensitivity of the FMIR technique is the availability of both sides of the plate for contracting the sample. When only a small amount of fiber is available, the fiber should be divided so as to provide sample for both sides of the plate. This is especially important when smooth pads such as polystyrene are scanned. The absorbance of the polystyrene band near 1495 cm.$^{-1}$ increases from 0.16 to 0.96 by
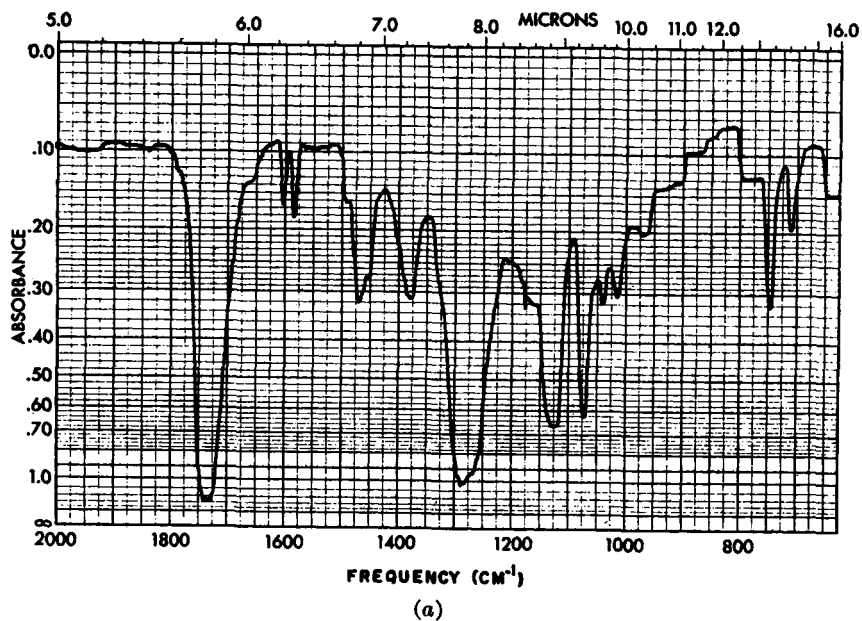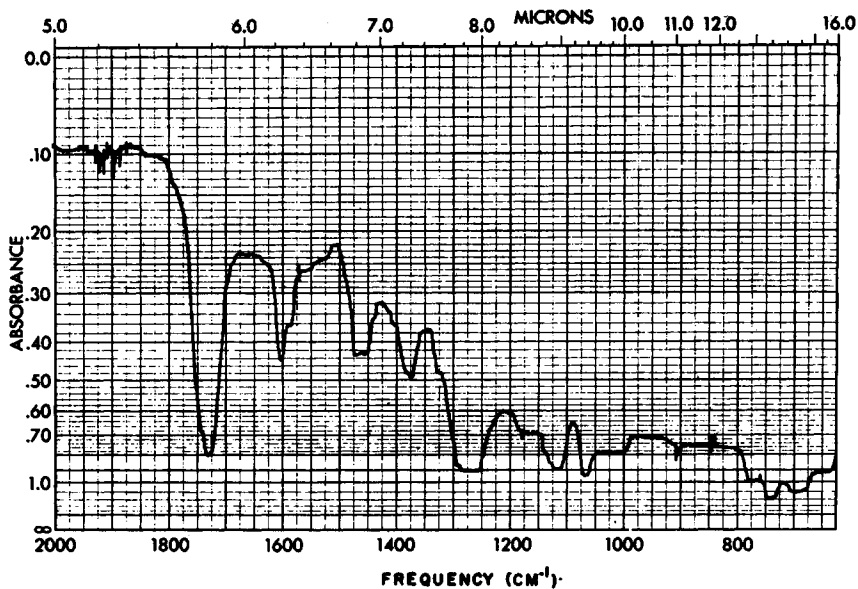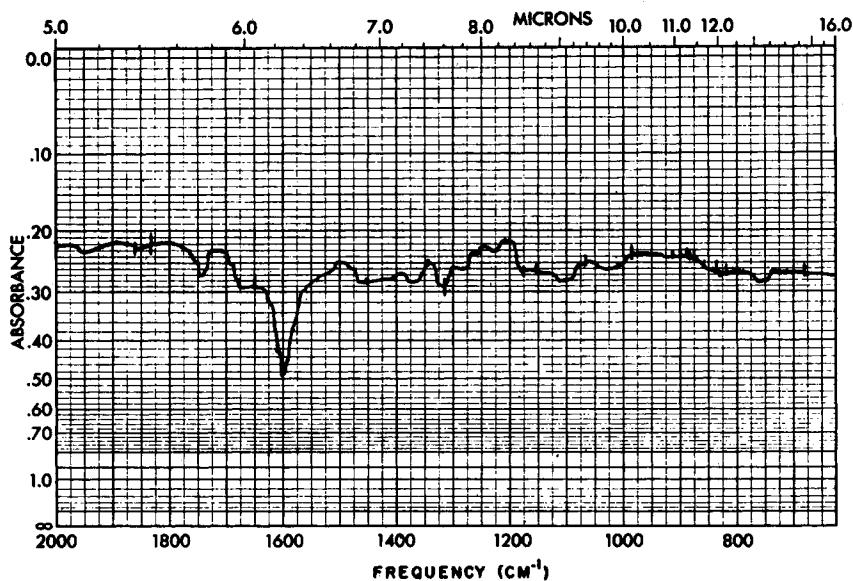
(a)

(b)

Figure 2. See caption p. 3959.

placing the same amount of material on both sides of the plate rather than on one side. The increase in sensitivity obtained by placing the sample against both sides of the plate is attributed to the greater amount of sample available for penetration by radiation as reflections occur internally from both surfaces.

(c)

(d)

Fig. 2. (a) FMIR spectrum of the linseed oil-type polymer;   (b) FMIR spectrum of polymer electrodeposited on mild steel, 1 μ thick;   (c) FMIR spectrum of polymer electrodeposited on mild steel, 0.5 μ thick;   (d) FMIR spectrum of polymer electrodeposited on mild steel, <0.1 μ thick.

The sensitivity of the FMIR technique increases as the pressure on the sample increases. The effect of pressure on sensitivity may be attributed to an increase in sample–plate contact and therefore to an increase in absorption. However, most of the samples require only sufficient pressure to hold the fibers firmly against the FMIR plate and high pressures are not required.

The malleability of the sample also affects sensitivity. The easier a sample deforms under pressure, the more sample–plate contact is achieved. Prepressing or powdering relatively hard fibers aids in producing better spectra and also aids in preventing deformation of the KRS-5 plate by the sample.

Sensitivity of the FMIR technique is also dependent on the index of refraction of the plate. As the index of refraction of the FMIR plate approaches but remains larger than that of the coating, the absorption bands become more intense. This increased absorption is attributed to the increased energy exchange between the plate and the sample. The silver chloride, KRS-5, and germanium plates employed in this study have indices of refraction of about 2.0, 2.4, and 4.0, respectively. The strongest FMIR spectra were produced with the silver chloride plate. However, KRS-5 is generally more useful for the FMIR technique, as it does not decompose as easily as silver chloride. Germanium generally produces relatively weak spectra.

For samples which are difficult to place in optical contact with the internal reflection plate, carbon disulfide or a liquid of relatively high index of refraction, such as methylene iodide, may be placed at the sample–plate interface.

Conclusions

The FMIR technique undoubtedly should be applied to many similar problems because (1) the FMIR technique shows great promise for lowering the limit of sensitivity in the infrared region; (2) FMIR spectra can be used directly in combination with collections of standard transmission spectra; and (3) the FMIR technique can be applied to the study of surface layers of arbitrary thickness.

References

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Résumé

La technique FMIR offre un moyen nouveau et amélioré d'identifier les enduits sur les fibres, pour élucider les liens entre les enduits et substrats et pour déterminer la nature des sites d'absorption des substrats au moyen de la spectroscopie infra-rouge. Cette technique est basée sur la réflexion interne de la radiation dans la région infra-rouge moyenne. La possibilité d'obtenir des spectres infra-rouges des matériaux ue

surface sans enlever les matériaus de ses fibree fournit dans la technique FMIR un avantage notoire par rapport aux techniques par transmission.

Zusammenfassung

Die FMIR-Methode liefert ein neues und verbessertes Mittel zur Identifizierung von Überzügen auf Fasern, zur Aufklärung der Überzug- und Substratbindungen und zur Bestimmung der Natur der Absorptionsstellen auf Substraten durch Infrarotspektroskopie. Dieses Verfahren beruht auf der inneren Strahlungsreflexion im mittleren Infrarotbereich. Die Fähigkeit Infrarotspektren von Oberflächenstoffen ohne Entfernung der Stoffe von der Faser zu erhalten, verleiht der FMIR-Methode eine bemerkenswerte Überlegenheit über Transmissionsmethoden.