Nondestructive Evaluation of Polymer Coatings by Mirage–FTIR Spectroscopy: A Tool for Surface Characterization

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ABSTRACT: We demonstrate the unusual applications of the recently developed mirage–Fourier transform infrared (FTIR) spectroscopy for nondestructive characterization of polymer coatings, especially on absorbing substrates or very thin coatings, where conventional FTIR techniques tend to fail. The mirage–FTIR has been briefly described. A few specific examples have been given to demonstrate the potential of this technique as a tool for surface characterization. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 1249–1252, 1998

Key words: nondestructive; surface coating; mirage–Fourier transform infrared spectroscopy

INTRODUCTION

Polymer coatings on materials are now routinely applied because of their ability to provide a protective cover, which extends their life/performance, protects them from environmental exposure, and provides a barrier to avoid contact between the container and containee. These qualities have led to the extensive use of polymer-coated materials, both in our day to day life (e.g., food packaging materials) and in several industrial applications. Such applications, in turn, require stringent quality specifications, both in terms of their identification and interfacial adhesion. In view of their thin and mostly transparent/scattering nature, nondestructive characterization of these coatings is difficult, especially when the coating itself is black or absorbing or is applied on absorbing substrates.

Modern FTIR spectroscopy, along with its sampling techniques, like attenuated total reflection (ATR) or diffuse reflectance infrared Fourier transform (DRIFT) have been used in some of the cases[1,2]; however, they fail to yield meaningful results when it comes to black or absorbing coatings or their substrate and/or very thin coatings. The photoacoustic–Fourier transform infrared (PA–FTIR) spectroscopy[3] has also been used in a few cases, but this also has limitations in terms of sensitivity and sample size. In an attempt to overcome this problem, we have used a recently developed the mirage–FTIR combination setup[4] and present the results with special reference to such coatings that are not possible by conventionally available methods. The technique provides a noncontact and nondestructive evaluation method for such special coatings. The technique, however, is equally useful for bulk analysis too.

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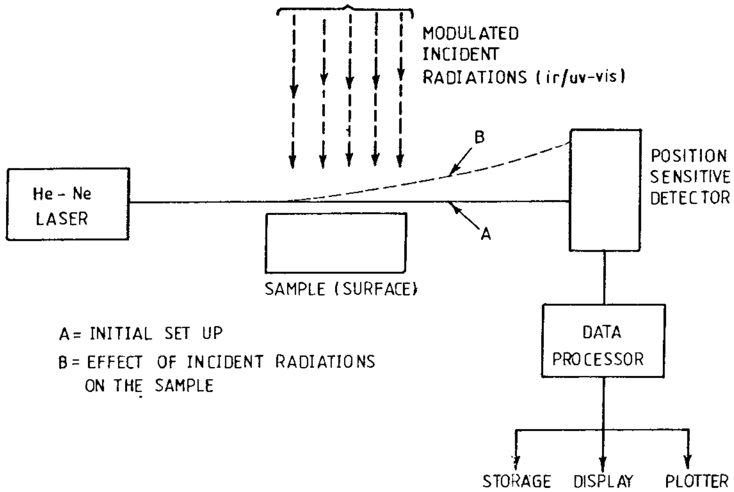

Figure 1 The principle of mirage spectroscopy.

MIRAGE SPECTROSCOPY

Recently, a new class of spectroscopy called photothermal spectroscopy, based on the principle of measuring a small rise in temperature associated with the absorption of electromagenetic radiation is being developed and exploited. Mirage spectroscopy[5,6] involves measurement of the deflection of a light beam as a result of the change of the refractive index of a medium as shown in Figure 1. When a sample is exposed to the modulated electromagnetic radiation, the nonradiative de-excitation causes heating of the sample, which, in turn, leads to a change in the refractive index of the surrounding medium and results in deflection of the probe beam passing along the sample surface. The extent of deflection of the probe beam is measured by a position sensitive detector, which can provide valuable information about (1) the thermal characteristic of the sample or surface and (2) spectroscopic characteristics,[7] depending upon the nature of the heating/incident beam. Theoretically, the probe beam deflection θ in the medium over a sample length L can be described as follows:[8]

$$\theta = \frac{L}{n}\frac{dn}{dT}\frac{dT}{dx}$$

where n is the refractive index of the medium, dT/dx is the temperature gradient, and dn/dT is the refractive index temperature coefficient.

Calculation of the beam deflection thus requires data on thermal gradient as well as the refractive index temperature coefficient. However, for spectroscopic applications,[7] the extent of deflection, which is a measure of the spectral absorption characteristics of the sample, is directly used as the detector output.

EXPERIMENTAL

Sample

IR spectra of the different types of coatings on following substrates have been recorded: (1) metal, (2) polymer, and (3) carbon fiber mesh.

Recording of IR Spectra

Mirage spectroscopy is a relatively new technique that has achieved the distinction of being a noncontact method suitable for surfaces and high-absorptivity materials. This basic characteristic led us to consider the possibility of combining it with a commercial FTIR spectrometer, replacing the detector output of the instrument with that of the mirage cell, and the highly monochromatic laser heating beam by a multichromatic IR source (through the Michelson interferometer). Although there had been several problems in synchronizing the mirage cell output with that of the FTIR detector, we succeeded in achieving a well-synchronized combination between a mirage cell and the FTIR spectrometer. Two models, namely IFS-66 (bench top models with simple optics/electronics) with some modifications and a highly so-

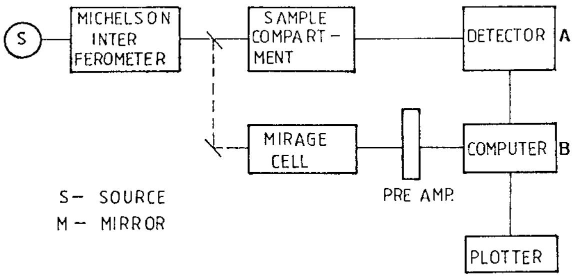

Figure 2 Line diagram of experimental setup for (a) FTIR and (b) mirage–FTIR measurement.

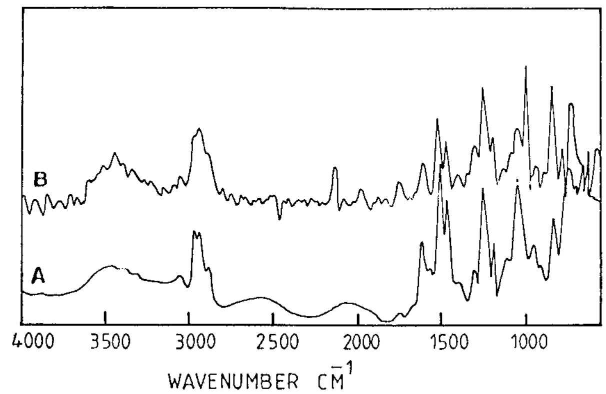

Figure 3 IR spectra of polymer coating on Al substrate (a) drift and (b) mirage–FTIR.

phisticated (more complicated) IFS-113V model from Bruker, Karlsruhe, Germany, have been tested for compatibility; but any other FTIR instrument can also be used for this.

The line diagram of the experimental setup showing the the mirage cell in the FTIR spectrometer (IFS-113V Bruker) is shown in Figure 2. The probe beam is aligned along the sample surface with the help of an oscilloscope or a lock-in amplifier. The optically aligned system has been used to record the spectrum of the sample. Spectral measurements were made at a resolution of 8 cm^{-1} and mirror velocity of 0.059 cm/s. The signal amplification was done by using a very low noise voltage preamplifier (SR-60, M/S Stanford Research System, USA). The absorption spectrum was obtained by ratioing the sample spectrum with that of the reference (a high-absorptivity black sample).

The DRIFT spectra were recorded using Praying Mantis model diffuse reflectance attachment with FTIR spectrometer under vacuum.

RESULTS AND DISCUSSION

Validation

Since mirage–FTIR has been used for the first time for recording IR spectrum of polymer coatings, it was necessary to compare the IR spectral features obtained by the present technique and those reported/obtained by another available method. For this purpose, the IR spectrum of polymer coating on an aluminum substrate was recorded by mirage–FTIR and DRIFT techniques.[9] The various characteristics bands, i.e., equal to 736 and 830 (epoxide vibrations), 2962 (CH stretching), and 1462 cm^{-1} (CH bending), etc., were found to be present at the same positions in both mirage–FTIR and DRIFT spectra, as shown in Figure 3. The excellent reproducibility and peak-to-peak matching of the IR spectra obtained by these two techniques (Fig. 3) confirmed the validity of the mirage–FTIR technique.

Analysis of Unknown Samples

Polymer Coating on Polymer Substrate

A measuring calibration plastic tape was used to record the IR spectrum of the coating. Initially, IR spectrum was recorded using DRIFT. The spectral features clearly indicated the contribution both from the coating and the polymer substrate, as shown in Figure 4(a). The DRIFT technique is unable to filter off the contribution of the substrate from the film (because of very thin surface coating).

The IR spectrum of the same sample when recorded using the present mirage–FTIR technique

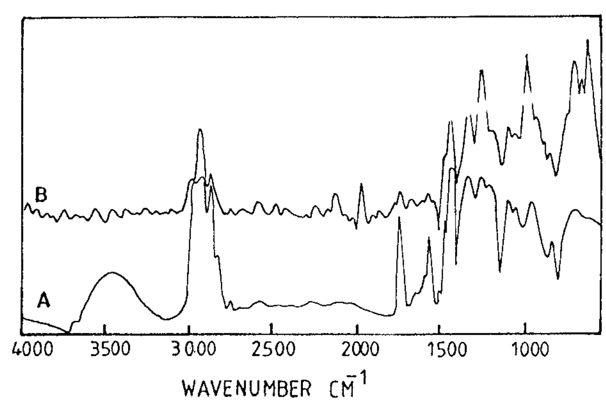

Figure 4 IR spectra of polymer coating on polymer substrate (a) drift and (b) mirage–FTIR.

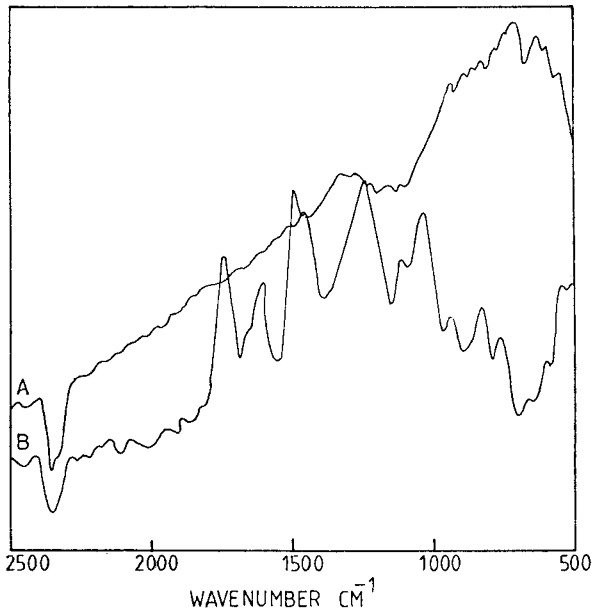

Figure 5 Mirage FTIR spectra of (a) substrate CF and (b) coated substrate CF.

showed characteristic features of the coating exclusively, as is evident from Figure 4(b). The spectrum of polymer coating [Fig. 4(b)] matches well with the spectrum of polyvinylchloride (PVC), for example, the characteristic bands equal to 610 and 1105 cm^{-1} due to C—Cl and C—C stretching, respectively. This spectral analysis indicated that coating was a PVC-based formulation. The spectral analysis of the DRIFT spectrum in the light of information obtained from the mirage–FTIR spectrum [Fig. 4(a) and (b)] leads us to conclude that the substrate was an acrylate-based formulation. It may be mentioned here that the mirage–FTIR is equally good for bulk sample analysis as well. This is an example of the application clearly demonstrating the characterization of film and substrate unambiguously. Conventional methods are not able to distinguish between the film and substrate.

Carbon Fiber Mesh

It is well established that most of the techniques tend to fail when it comes to highly absorbing (e.g., black) samples.[10] The present technique was used to obtain IR spectrum of the coating on a black carbon fiber mesh (substrate). The IR spectrum of the substrate with and without coating were recorded and are shown in Figure 5. Even visual comparison of the two spectra indicates that there is no contribution from the black mesh (substrate) in the spectrum of coating recorded directly. The spectral analysis indicated that coating was an epoxy-based formulation.

CONCLUSIONS

The present work is an attempt to demonstrate the application of the mirage–FTIR technique for contactless and nondestructive evaluation of surface coatings, irrespective of the substrate. The technique is excellent for the evaluation on black substrate, which is difficult to analyze.

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