Measurement of Cure in Optical Fiber Coatings by Infrared Microspectroscopy

J. D. LOUDEN

Analytical and Physical Sciences Research and Technology Department, ICI Chemical & Polymers Ltd., PO Box 8 The Heath, Runcorn, Cheshire WA7 4QD, England

SYNOPSIS

A method suitable for measuring the state of cure in acrylate optical fiber coatings is described. Both the outermost (secondary) and the innermost (primary) coatings cure states can be determined. The method is reproducible and suitable for manufacturing process control and quality control in produced fiber. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Coatings are applied to a freshly produced optical fiber as soon as possible after drawing has taken place because of the vulnerability of the fiber. Resin formulations can contribute to the strength retention of the fiber in two ways: by providing protection from mechanical abrasion or mechanical abuse and by delaying hydrolytic attack at the glass surface, thereby reducing the effects of stress corrosion. There are three potential coating systems available: thermally cured silicones[1]; ultraviolet (UV) cured acrylates[2]; and hot melt thermoplastics.[3] Of these three it is the acrylate type that is of interest here and this article deals solely with the UV cured acrylates.

Coating systems generally consist of two layers of UV cured acrylate, although there are systems that consist of four layers. The inner (primary) layer is of a lower modulus than the outer (secondary) layer and its main function is to provide resistance to microbending over the operating range of the cable. The secondary layer increases overall flexural strength and dissipates lateral external forces. It also acts as a protection against mechanical damage encountered in cabling operations.[4] The state of cure of the layers is one of the most important parameters of the coatings as this affects a number of its physical properties, including hydrogen generation, extractable materials, and water absorption.

This article describes the work that has been done in developing a method to measure the state of cure of acrylate coatings on production fiber. The technique of Fourier Transform infrared (FTIR) microspectroscopy is used to determine the state of cure on all the acrylate polymer coatings surrounding an optical fiber.

Previous reports on measuring cure on optical fibers by IR spectroscopy related to measuring the cure on the secondary layer only using multiple internal reflection spectroscopy, and then only on the top few microns of the layer.

EXPERIMENTAL

Samples of uncured secondary and primary resins, cured films of these two resins, and an optical fiber coated with these resins were obtained for analysis. The IR spectra of the acrylate coatings on the optical fiber were recorded on an AIRE Scientific IR microscope interfaced to a Nicolet 510 FTIR spectrometer. The spectra of the reference materials were recorded in the main sample compartment. All spectra were recorded over the range 4000–650 cm^{-1} with a resolution of 4 cm^{-1}. In a typical microscope experiment, 500 scans were

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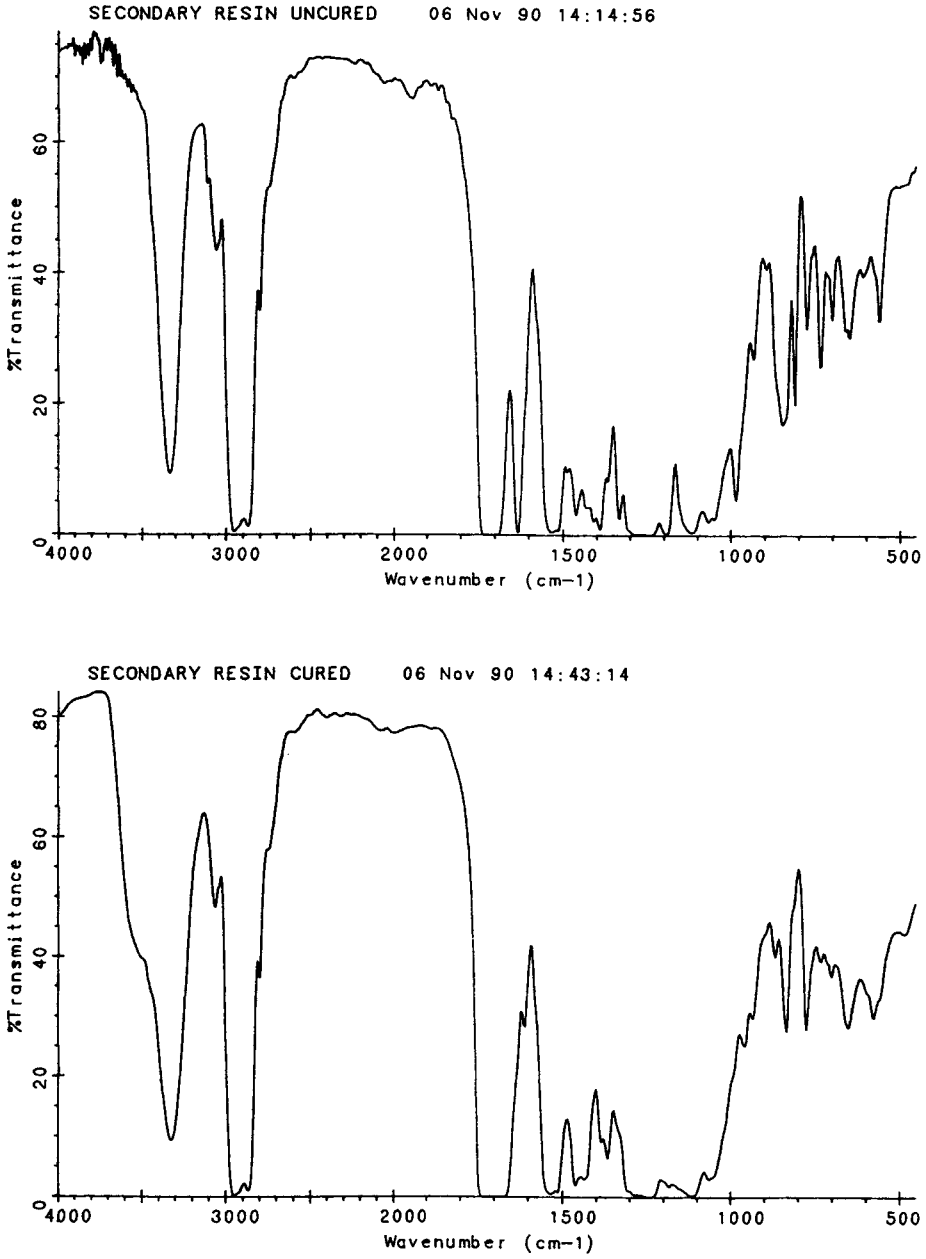

Figure 1 Secondary resin uncured and cured (full spectrum).

averaged to achieve a satisfactory signal-to-noise ratio.

Measurements on Reference Materials

The resin sample was simply squeezed between two KBr windows and the spectrum run in the sample compartment of the spectrometer. The cured resin samples were held over a suitable aperture and the spectrum run in the sample compartment of the spectrometer.

Measurement on Fiber Coatings

For the coatings on the optical fiber it was necessary to strip the two coatings off the fiber. To do this a sharp scalpel blade was used to slice through the two coatings to the glass fiber and then drawn along

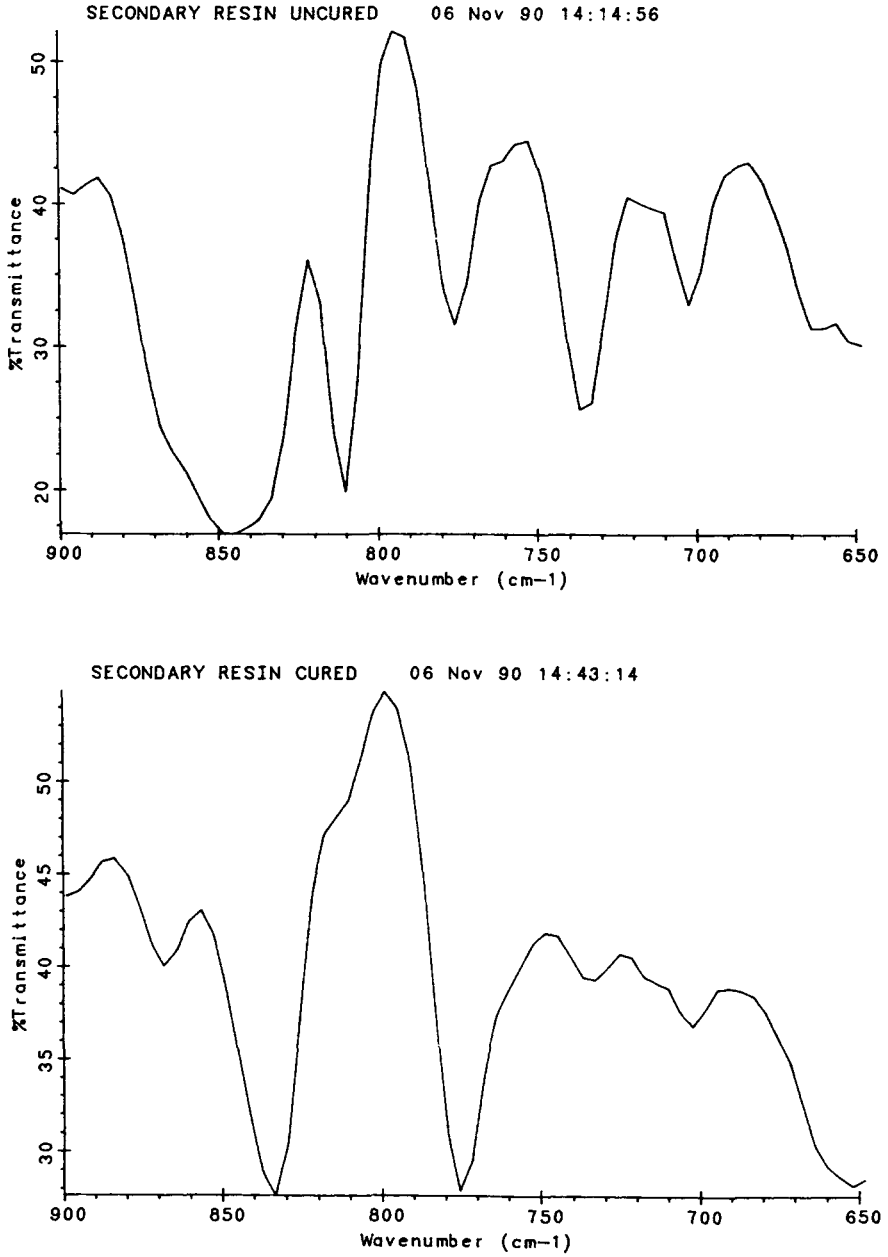

Figure 2 Secondary resin uncured and cured (900–650 cm^{-1}).

the fiber to obtain a length of cured material (3–5 mm). The soft primary coating was then separated from the hard secondary by holding the two coatings flat against a glass slide and the primary coating scraped from the secondary using the scalpel blade. The process was continued until all the primary coating had been scraped off and the secondary coating looked "clean" of primary.

A small piece of each coating was then mounted between KBr windows in a compression cell and the spectrum obtained on the IR microscope in transmission.

RESULTS AND DISCUSSION

IR spectroscopy involves the detection of vibrational, rotational, bending, and twisting motions of the atoms in a molecule. When a material is irradiated with IR light it will absorb certain wave-

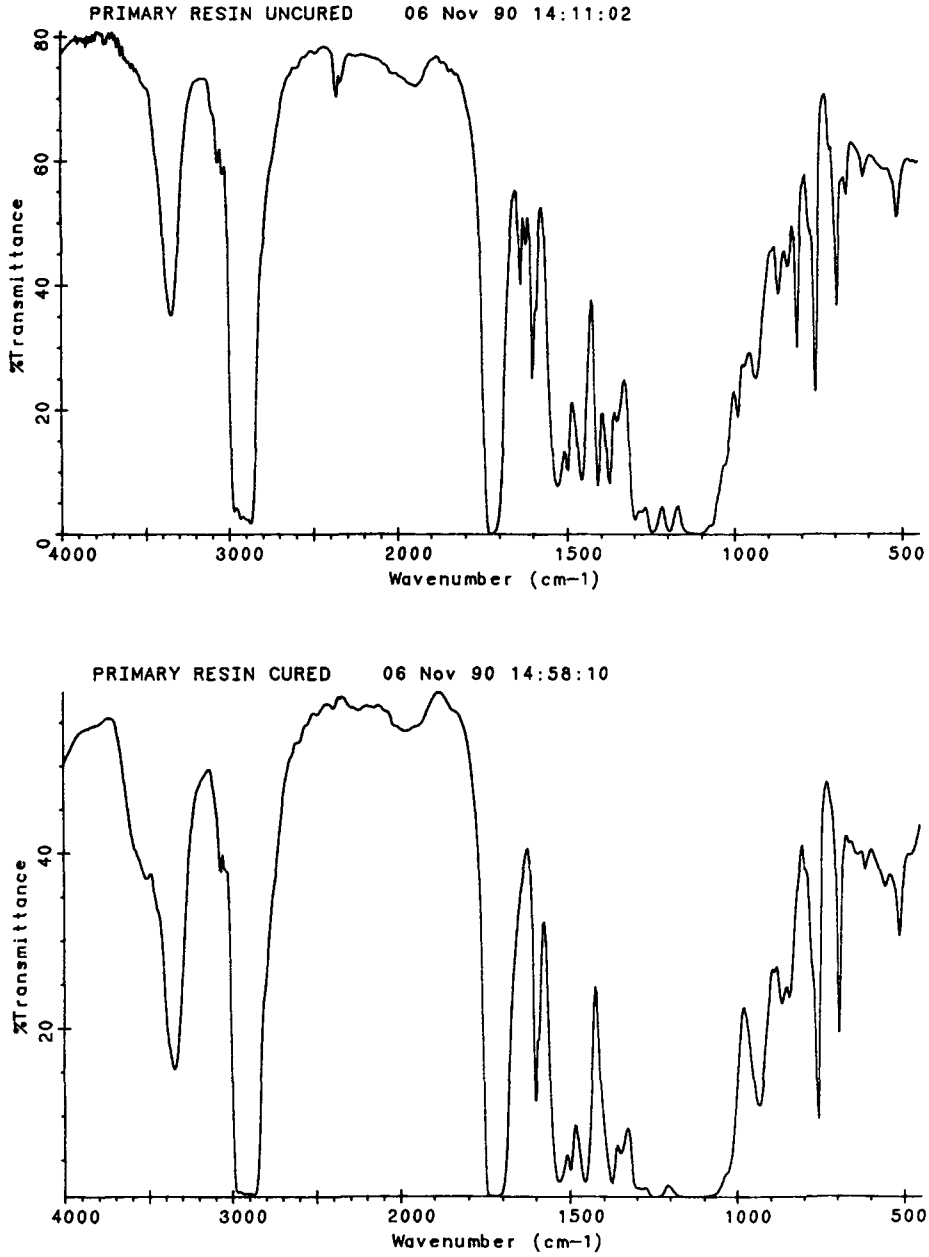

Figure 3 Primary resin uncured and cured (full spectrum).

lengths of the light. These absorptions are characteristic of functional groups comprising the molecule and the spectrum is a fingerprint of that particular molecule. Thus the presence of particular peaks in the spectrum provides information about the structure of the material. And peak intensities can be related directly to the concentration of individual bonds in the material.

The IR spectrum of secondary and primary resin in the uncured state and the "fully" cured state (obtained by curing free film samples with a Fusion Systems curing station) are shown in Figures 1 and 2, respectively. A number of spectral changes are apparent between the two states.

The peaks selected to monitor the cure reaction need to fulfill two criteria:

1. it needs to be associated with a known change in chemical structure and
2. the intensity of the peak needs to be in the dynamic range of the spectrometer.

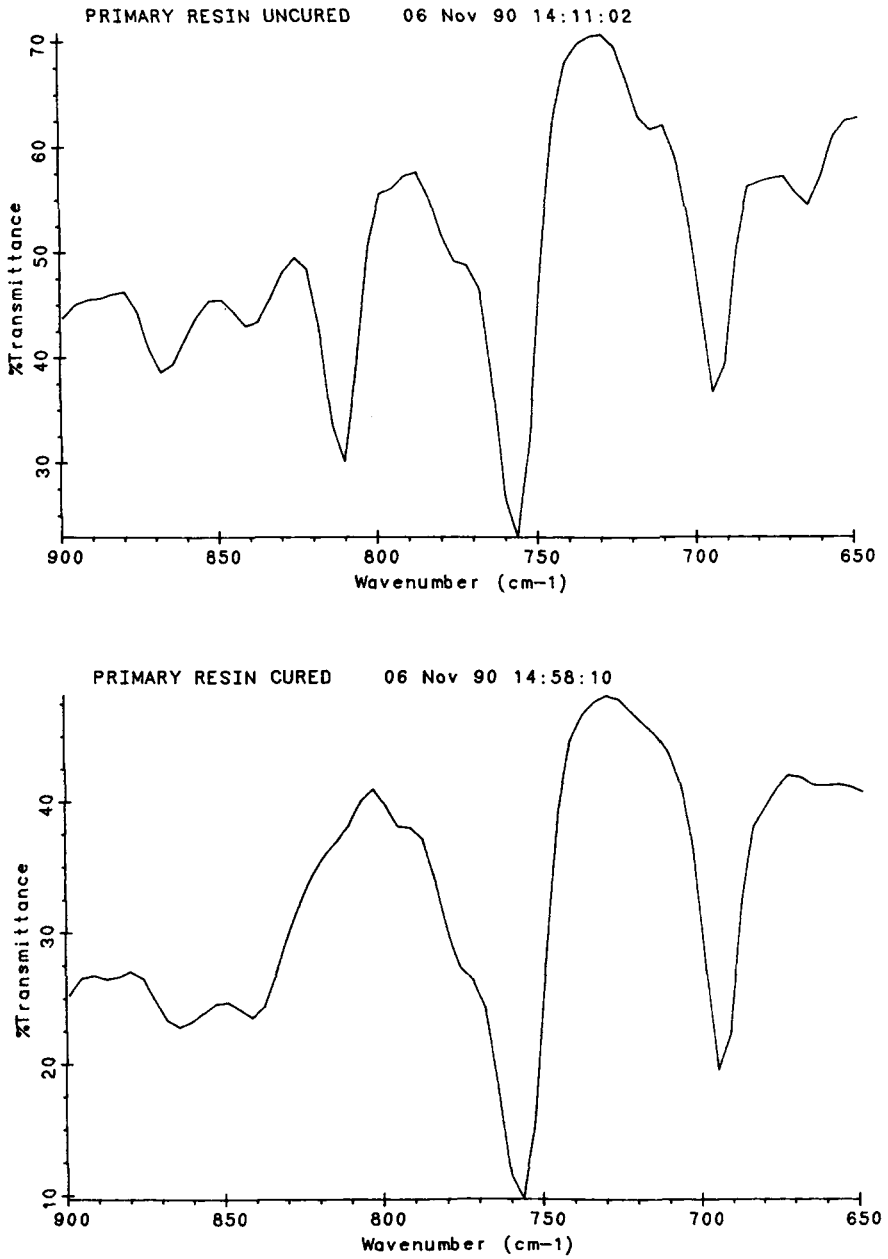

Figure 4 Primary resin uncured and cured (900–650 cm^{-1}).

Two such peaks are the C=C stretching vibration at 1640 cm^{-1} and the C—H deformation vibration on the acrylate double bond at 810 cm^{-1}. For this determination the 810 cm^{-1} was chosen to follow the degree of cure. Figures 2 and 4 show the difference in the uncured and cured states of secondary and primary resins, respectively, in the spectral region of interest (900–650 cm^{-1}).

For the secondary the peak at 775 cm^{-1} is used as an internal standard and for the primary the peak at 755 cm^{-1} is used as an internal standard because these peaks are unaffected by the curing reaction.

Cure Calculation

The state of cure is calculated as a percentage using the following equation:

$$\% \text{ cure} = 1 - \frac{(\text{PR sample} - \text{PR fully cured})}{(\text{PR resin} - \text{PR fully cured})} \times 100$$

where PR sample is the peak ratio value for the production fiber coating, PR fully cured is the peak ratio value for the fully cured coating, and PR resin is the peak ratio value for the uncured resin.

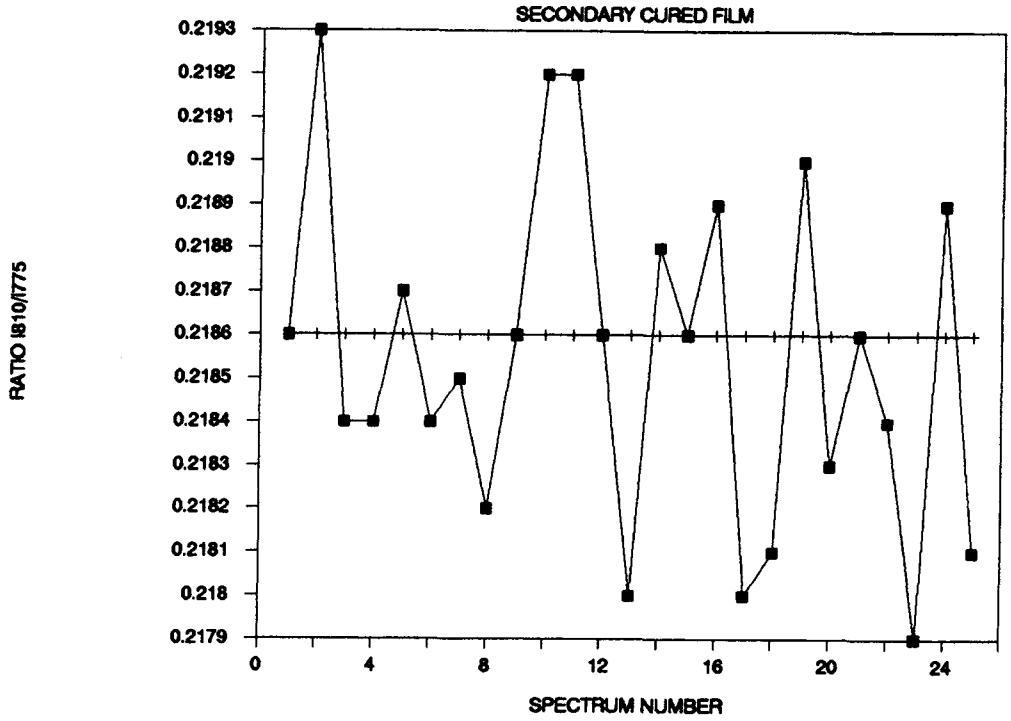

Figure 5 Main bench reproducibility/stability test.

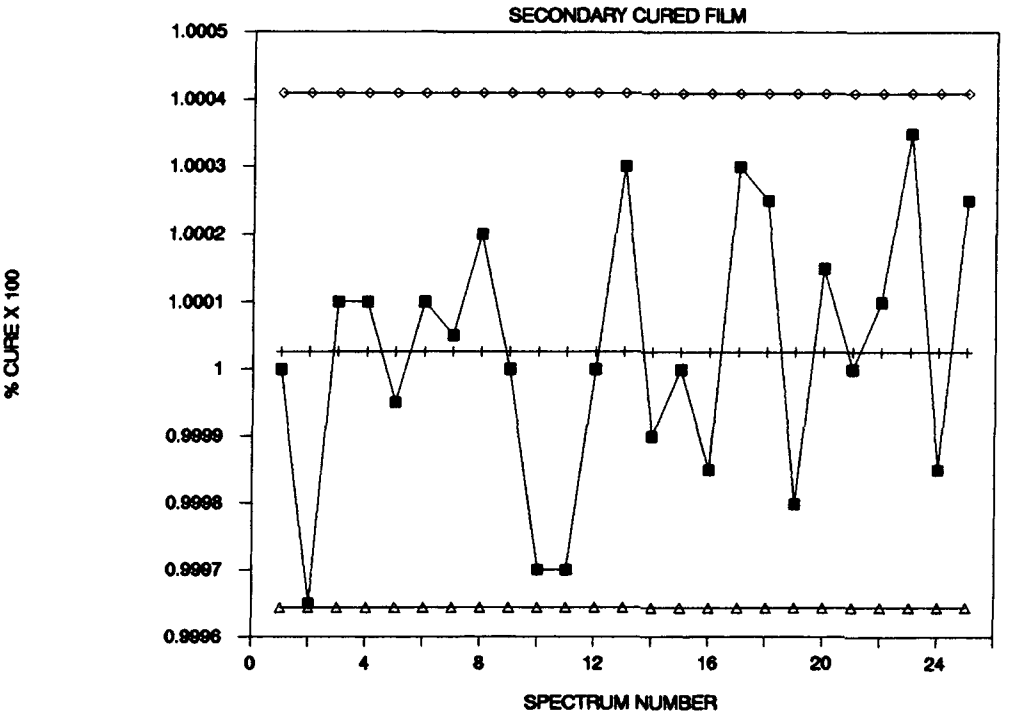

Figure 6 Main bench reproducibility/stability test.

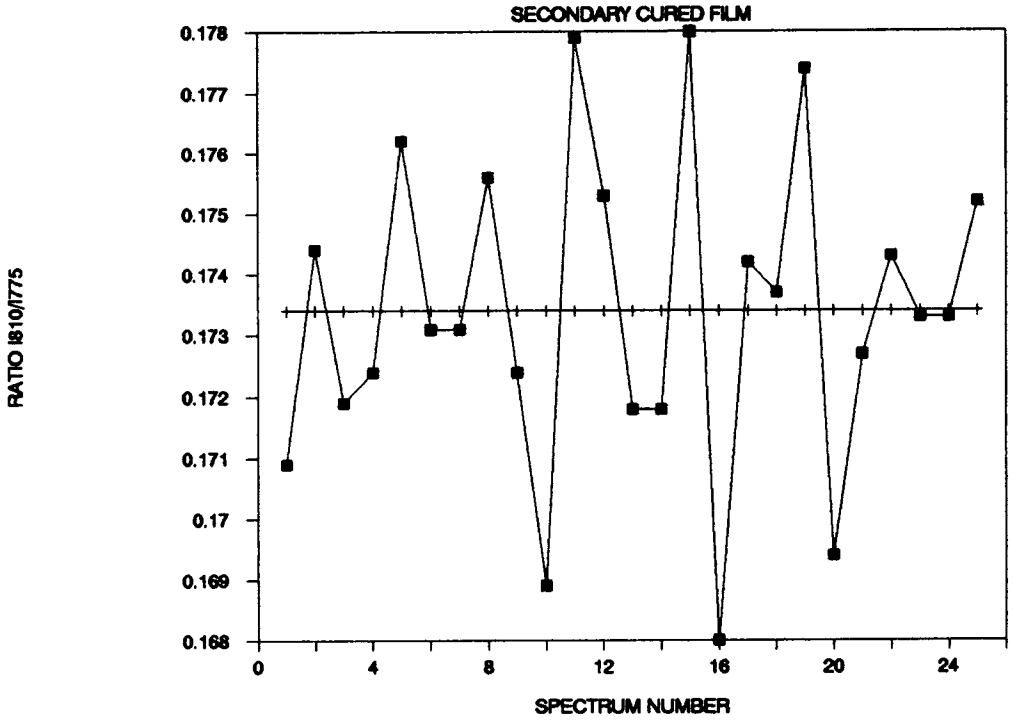

Figure 7 Microscope reproducibility/stability test.

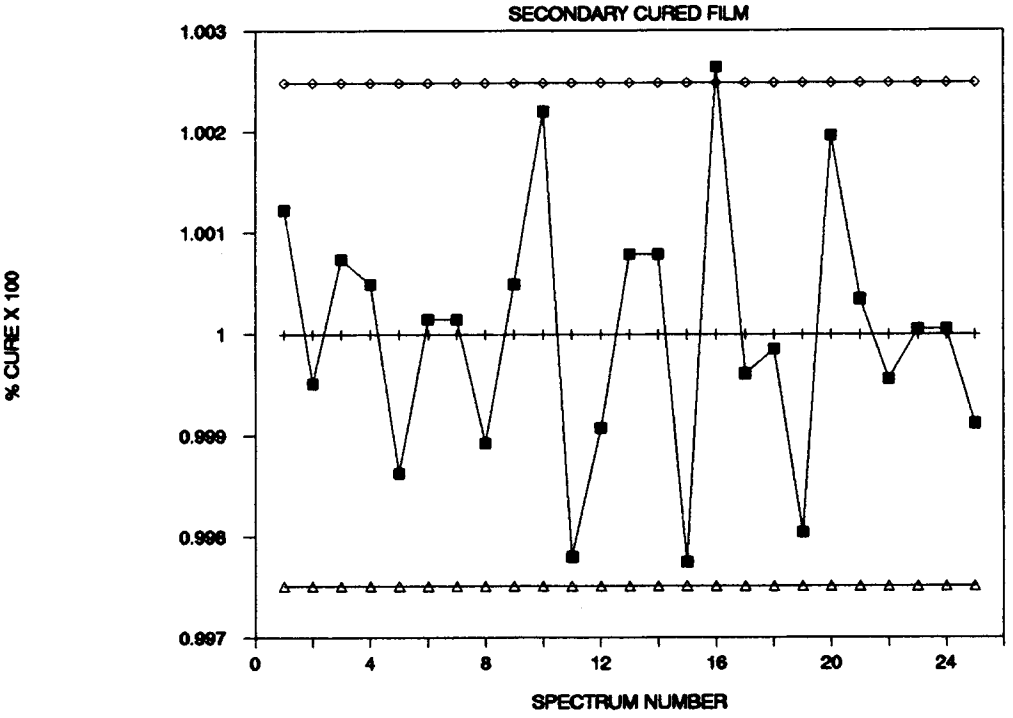

Figure 8 Microscope reproducibility/stability test.

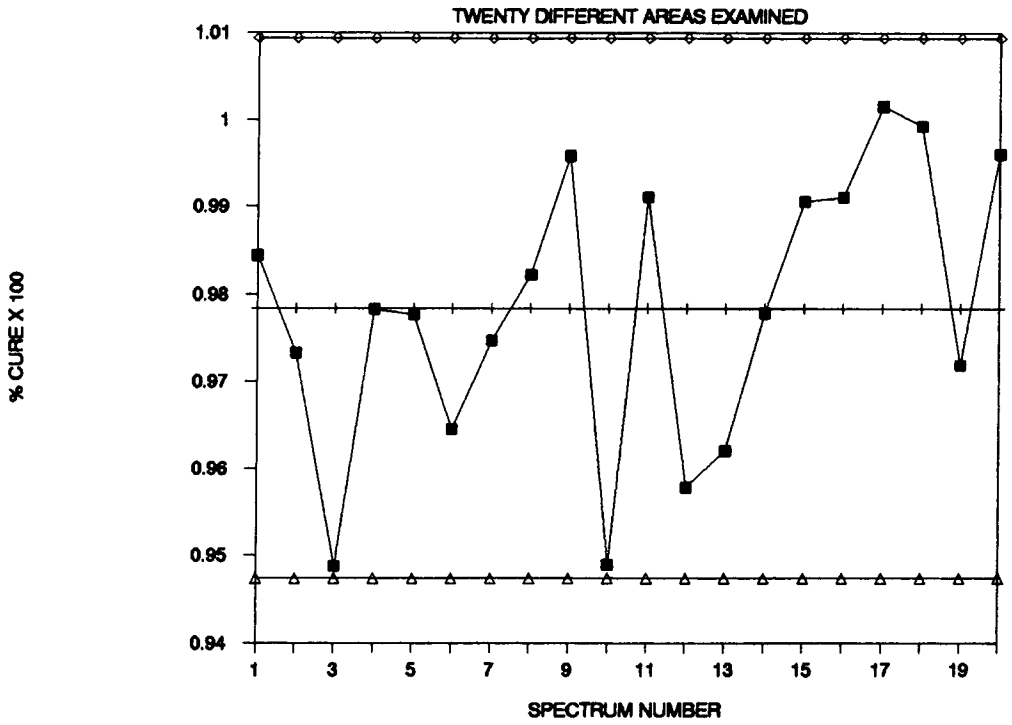

Figure 9 Percent cure on 20 areas of secondary fully cured film.

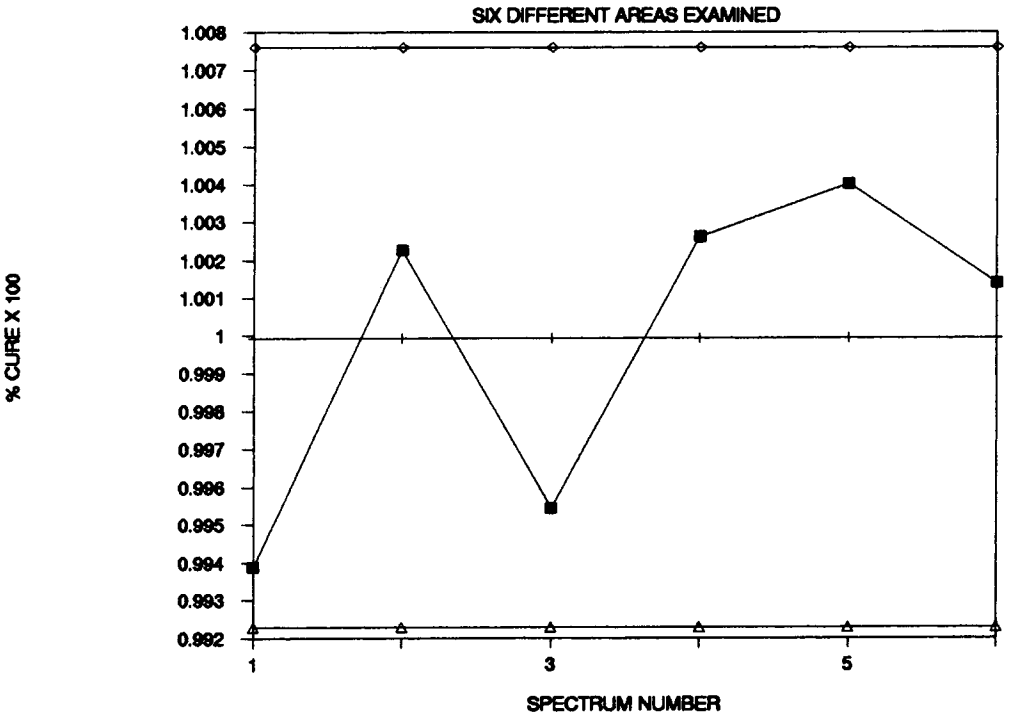

Figure 10 Percent cure on six areas of primary fully cured film.

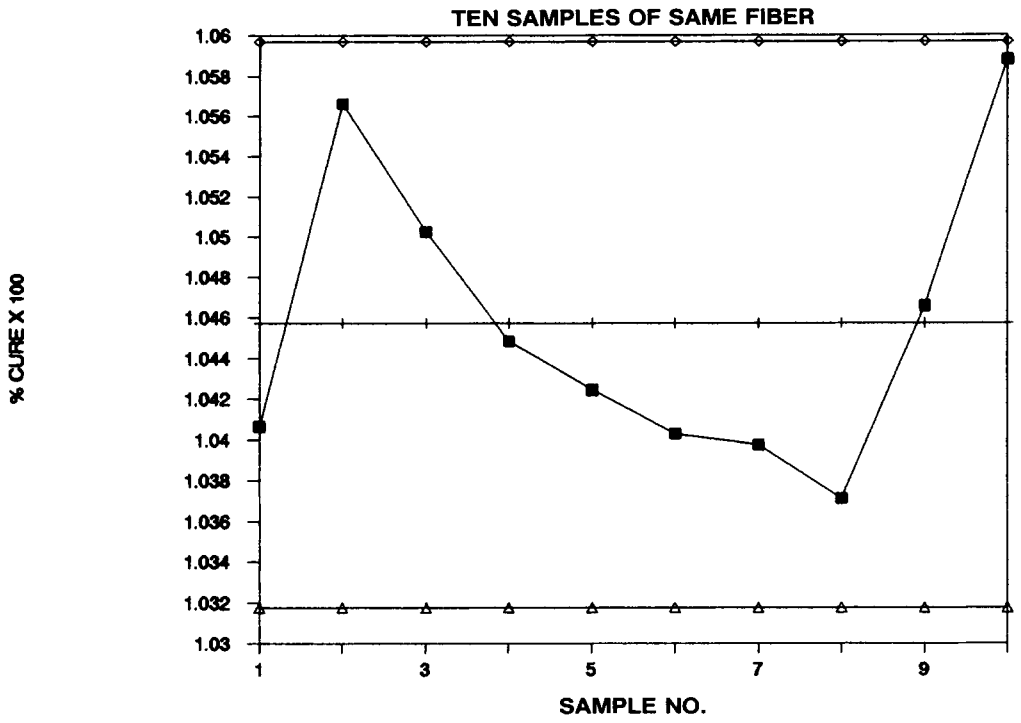

Figure 11 Percent cure of secondary coating on optical fiber.

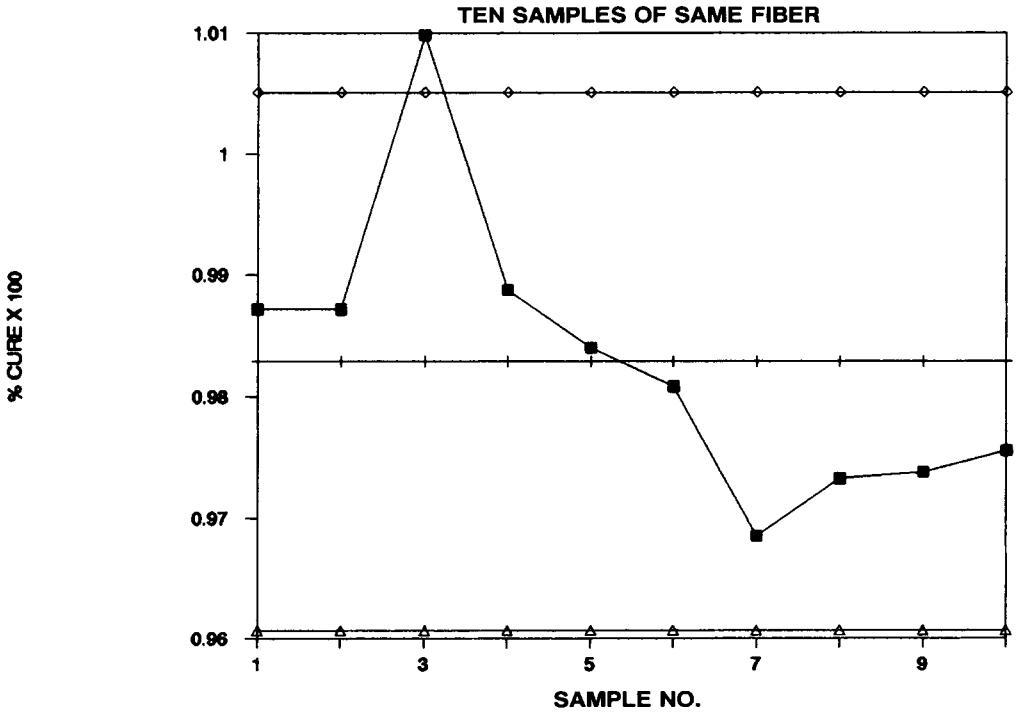

Figure 12 Percent cure of primary coating on optical fiber.

Main Bench Reproducibility/Stability Test

In order to determine the reproducibility/stability of the main FTIR bench, a piece of secondary fully cured film was placed in the sample compartment and 25 consecutive spectra taken. The results are shown graphically in Figures 5 and 6. Figure 5 is the ratio of the two peaks 811/775 against number of spectra taken, and Figure 6 shows this variation as percent cure against spectrum number. The average value is 100.003, standard deviation 0.02.

Microscope Reproducibility/Stability Test

To determine the reproducibility/stability of the FTIR microscope, a piece of secondary fully cured film was placed on the microscope sample stage and accurately positioned using the stepper motor controlled sample stage. For this test a sample spectrum was taken, then a background spectrum was taken and this was repeated 25 times. The sample was accurately repositioned in the same place by using the accuracy of the sample stage. Figures 7 and 8 show these results graphically. Figure 7 shows the ratio of the peaks 811/775 against the spectrum number and Figure 8 shows this variation as percent cure against the spectrum number. The average value is 99.996, standard deviation 0.12.

Repeatability of Measurement

Figure 9 shows graphically the percent cure for 20 different areas (approximately 50 mm^2) of the fully cured secondary film. It can clearly be seen that the film is not uniformly cured, values ranging from 97 to 102.5% cure, and this must be taken into account when using this as the standard for the percent cure determination on the fiber coatings, that is, it is necessary to determine the average cure of the standard by doing replicate measurements and using the average value in the calculation. The average value is 100.002, standard deviation 1.55.

Figure 10 shows the percent cure for six different areas of the fully cured primary film. The average value is 99.999, standard deviation 0.38.

Measurements on Optical Fiber Coatings

Figure 11 shows the percent cure for 10 samples taken from the secondary coating from an optical fiber. The average value is 104.573, standard deviation 0.69.

Figure 12 shows the percent cure for 10 samples taken from the primary coating from an optical fiber. The average value is 98.289, standard deviation 1.11.

The accuracy of each measurement is ±0.25% as shown by the microscope stability measurements, thus the measurements on the fiber samples with an accuracy of ±2% show that there is variation of cure along the fiber length.

Cure Measurement Benefits

The two main benefits of the measurement are in manufacturing process control and quality control. There are a number of factors that affect the cure in the coating. These can be equipment related (lamp/reflector efficiency and level of nitrogen inerting), or material related (resin absorptivity and cure efficiency). Cure measurements may be used to study process variables. On manufactured fibers cure measurements can be used as a quality control tool to ensure a consistent product.

CONCLUSIONS

Using FTIR microspectroscopy it is possible to measure the state of cure of the primary and secondary acrylate coatings on a manufactured optical fiber. The method measures the percent cure throughout the bulk of the two acrylate coatings because it is based upon a transmission measurement and not a reflection measurement. The method is reproducible and fairly quick. The multiple reflection technique is tedious because of sample preparation (preparing arrays of about 30 fibers) and then ensuring good contact with the MIR crystal, and only the top few microns of only the secondary (outermost) layer were examined.

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