Nanosampling Internal Reflection FT-IR Study of Polymer Filaments

This paper reports on the development of a new accessory which allows the infrared spectrum to be recorded by internal reflectance spectroscopy from nanogram and microgram samples. Specifically, spectra taken of the end of a 20-μm polyester filament, a 250-μm multicomponent acrylic fiber, and a 5-ng droplet of paraffin oil will be presented. Since the smallest filament is 20 μm, the calculated sample size is within the nanogram range.

Instrumental methods which allow routine, nondestructive characterization of ultrasmall samples (< 1 μg) help further advances in polymer physics, polymer chemistry, and polymer engineering. Reviews of the specific kind of information obtainable from the vibrational spectrum have been thoroughly presented by Koenig, Zerbi, and many others.[1-8] Molecular spectroscopic methods such as the Raman microprobe[9,10] and its counterpart in the infrared region[11] of the spectrum have warranted much attention.

Infrared microsampling is predominantly limited to transmission and reflectance modes. Unfortunately, these methods put limitations on the types of samples which can be studied easily. It seems logical to extend the tools of the polymer infrared spectroscopist to include nanosampling by internal reflection spectroscopy. In this way, some of the benefits of internal reflection spectroscopy[12] can be applied to the study of ultra-small samples.

It has long been realized that internal reflection spectroscopy has a number of important advantages over transmission in the area of microsampling.[13] These advantages include:

1. Ease of Preparation. It is only necessary to bring the sample in contact with or in close proximity to the sampling surface. In the single filament spectrum (Fig. 2), the end of the filament was brought into contact with the sampling surface.

2. Greater Spectral Contrast. By selecting the correct parameters [angle of incidence and refractive index of the internal reflection element (IRE)], the spectral contrast for a single reflection is greater than for a single transmission; hence, in principle, smaller samples can be examined by internal reflection spectroscopy (IRS).

3. No Interference Fringes in Internal Reflection Spectra. This is especially important for small samples where fringes obscure weak absorption bands.

Even though this potential was realized for many years, it is only now that practical problems, such as design of an IRE where light can be collected from micron size sampling areas, have been solved; thus, one is able to put to use the theoretical advantages.

By combining the appropriate optics, including specially designed internal reflection elements, a new nanosampling accessory has been designed which allows the spectrum of extremely small samples such as the diameter of a 20-μm poly (ethylene terephthalate) filament to be taken. Experimental details of the design of this attachment have been discussed elsewhere.[14]

All spectra were taken on a Mattson Sirius 100 Fourier transform infrared spectrometer equipped with a TGS detector interfaced to a Starlab computer. When the exiting aperture of the prism is masked to expose an area only sufficient to sample the 20-μm filament, a 1.0% throughput to the beam was measured. Forward and reverse velocities of the corner cube interferometer were kept at 2 cm/min and a single gain of 3 was used. To optimize the signal-to-noise ratio, 300 scans for sample and background files were accumulated and processed. Many fewer scans would be required with the aid of a mercury–cadmium–telluride detector.

The polyester fiber consisted of melt-spun PET which contained dilustrant and finish. This fiber was spun at a take-up speed of 3500 m/min. The larger multicomponent acrylic fiber had a 250-μm cross section. The paraffin oil droplet was placed on the tip of the prism by dipping the 20-μm filament into the oil, and then touching the wet fiber end to the prism tip.

A comparison of the nanosampling internal reflectance spectrum taken of the PET filament with its transmission spectrum taken with a 4X beam condensor (Accessory 4XTBC) is presented. The transmission spectrum is presented in Figure 1. Since the filament is 20 μm thick, in spite of good sensitivity, too many of the weak peaks near 3000 cm, the strong absorption bands at 1727,

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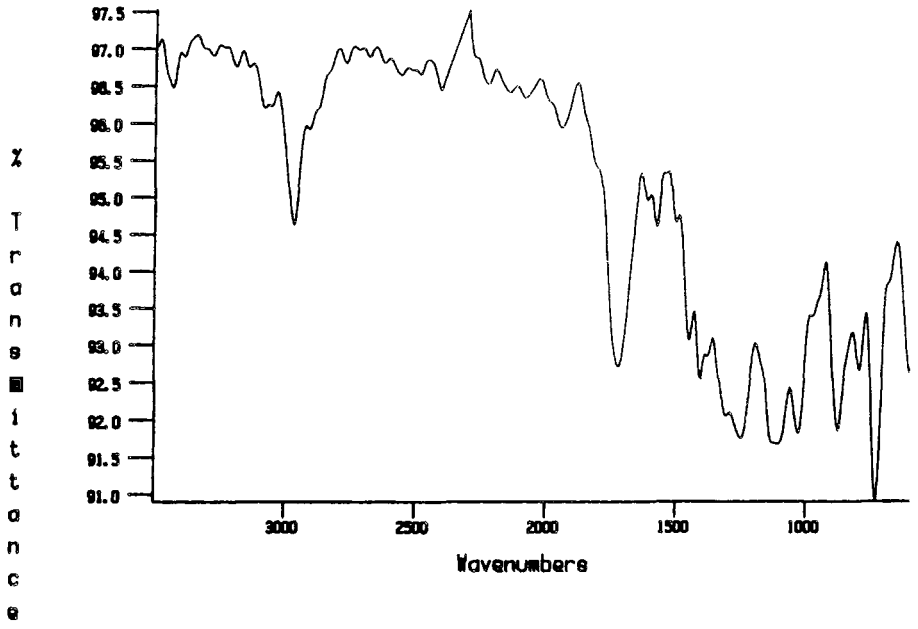

Fig. 1. Transmission spectrum of the 20-μm PET filament taken with a 4X beam condenser.

1263, and 1109 (carbonyl stretching, ester linkage stretch, and benzene C—H wagging with C—C breathing, respectively) suffer severe flattening, as if total absorption occurs over these bands.

In Figure 2, the internal reflection spectrum is presented which clearly exhibits sharper detail and resolution of the peaks in the spectrum. The spectral contrast shown by this nanosampling internal reflection accessory can then be applied to quantitatively characterize the molecular states of fibers which have been processed to tailor their microstructure.

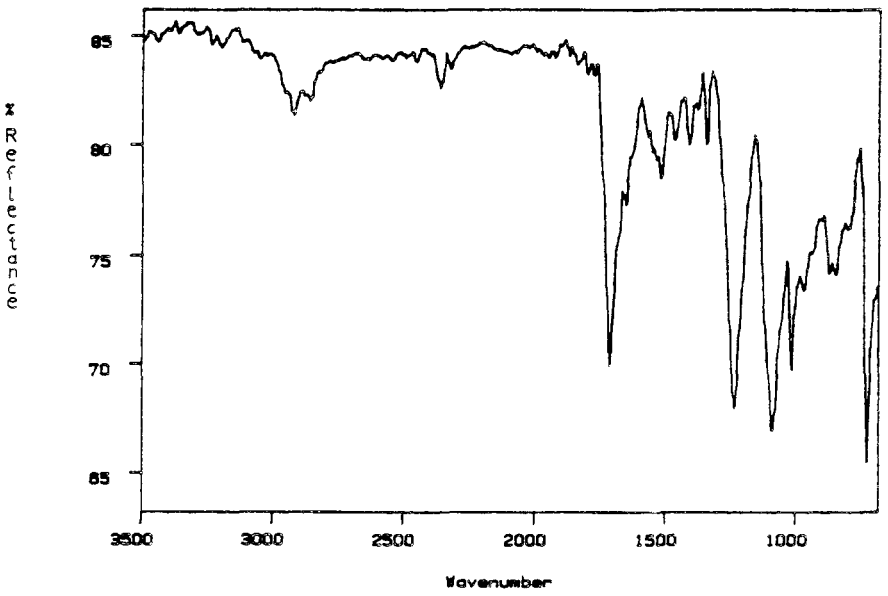

Fig. 2. Internal Reflectance spectrum of the end of a 20-μm micron PET filament.

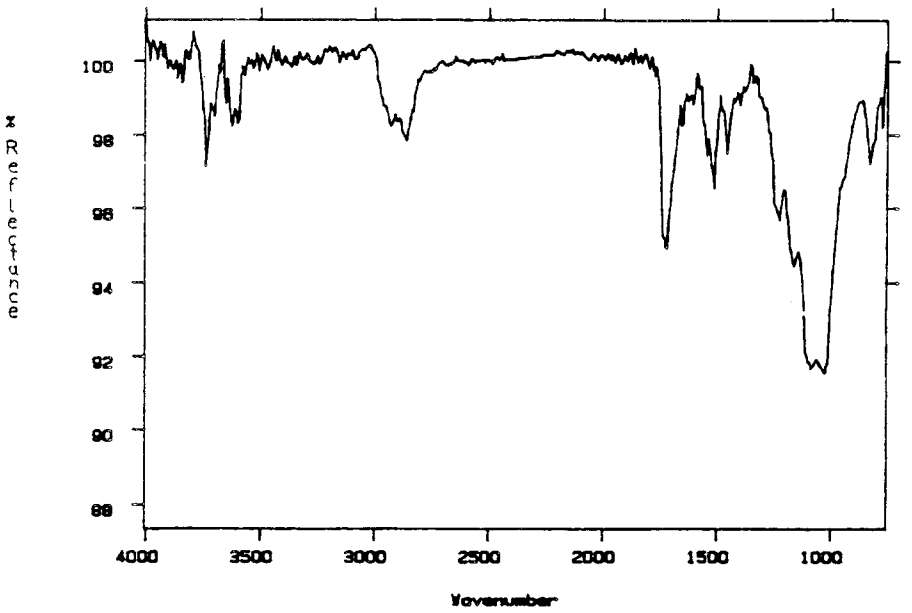

Fig. 3. Internal reflectance spectrum of the end of an acrylic optical fiber 250 μm.

Another example of the application of this accessory is presented in Figures 3 and 4, which give the spectrum of the multicomponent complex acrylic fiber from 3500 to 750 wave numbers. The spectrum in Figure 3 is of the entire fiber, while the spectrum in Figure 4 was taken with the mask partially closed, revealing the spectrum of a partial area of fiber cross section. Several features in the spectrum are substantially changed in relation to the relative absorptivities and the appearance of new peaks.

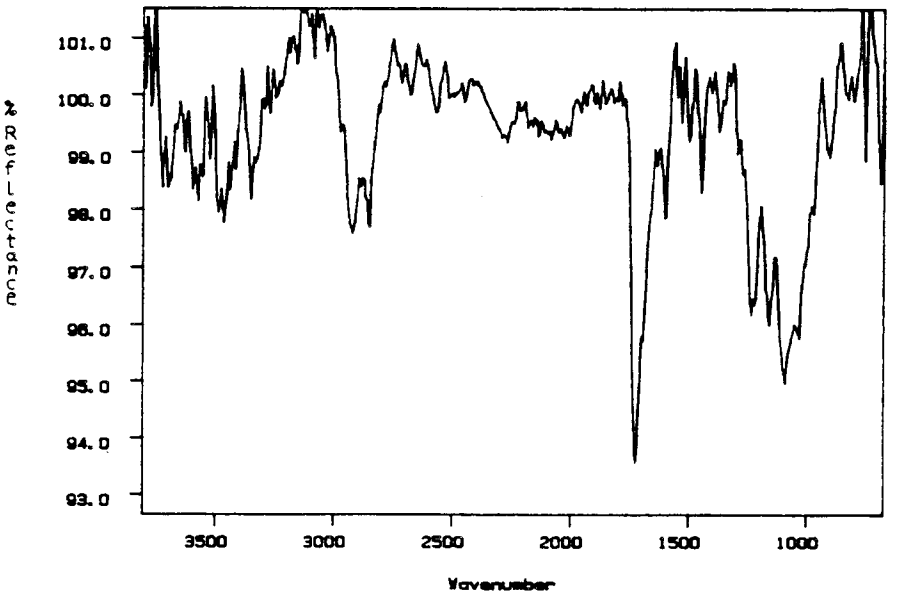

Fig. 4. Internal reflectance spectrum of the end of the acrylic fiber with 75% masking.

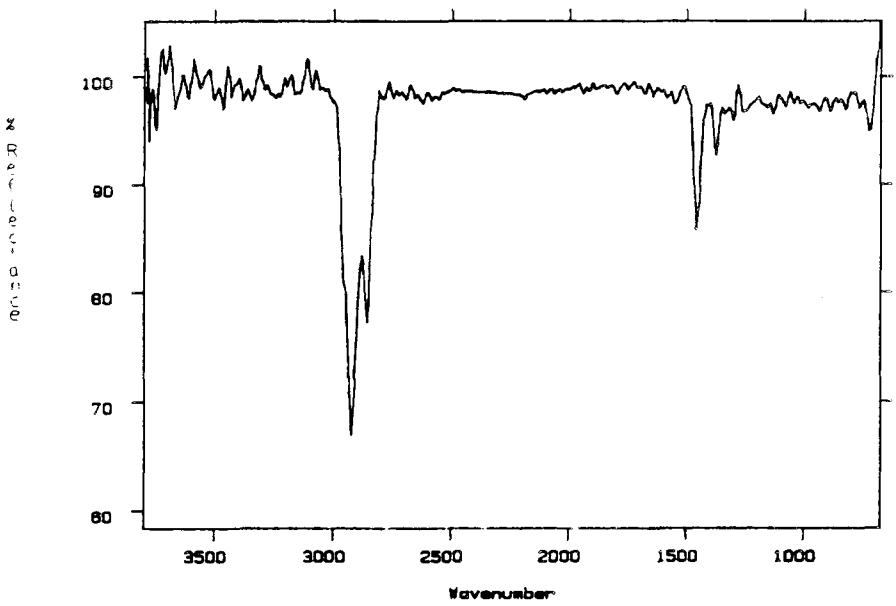

Fig. 5. Internal reflectance spectrum of a microdroplet of paraffin oil less than 20 μm.

Thus, it is possible to selectively study the internal reflectance spectrum of certain areas of the fiber's cross section without dissecting of disrupting the fiber in any way. As a final example of sensitivity, Figure 5 presents the spectrum of a microdroplet of paraffin oil (less than 20 μm in diameter) with a calculated weight of only 5 ng. The strong C—H stretching bands are clearly visible.

In summary, the accessory allows very sensitive internal reflection spectroscopy on extremely small samples to be carried out. It is also flexible in that by quick exchange of internal reflection elements, various types of samples from single filaments to multifilament yarns, composites, powders, and viscous polymer liquids even of nanoliter size can be sampled. This accessory can be used for the study of the diffusion of small molecular weight compounds in gels applied to the surface of the IRE. Polymer blending studies in which small spatial separation in characterization would be desirable is now possible. Finally microstructure characterization by nanosampling internal reflection, FT-IR, in general, should prove effective.

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