

Application to High Polymer Materials

Photoacoustic spectroscopy (PAS) is a method of obtaining the absorption spectrum of a substance by detecting and deconvoluting the periodic thermal changes occurring in the sample in the form of the acoustic signal generated by micropressure changes in the gas surrounding the substance in a closed chamber. The sample is irradiated by a monochromatic source which is modulated by the instrument's interferometer. The application of PAS in the infrared region is fairly new, and it has come to be studied in many fields along with the increasing popularity of Fourier transform infrared spectrophotometers. The features of PAS include the

Depth-Profiling

When analyzing in the depthwise direction using PAS, the depth information comes from the parameter called the thermal diffusion length which is a function of the thermal conductivity of the substance and the characteristics of the irradiating energy, etc. In a thermally thick sample, the photoacoustic signal becomes stronger in proportion to the thermal diffusion length. Since this thermal diffusion length depends on the irradiation modulation frequency, the depth of that portion of the sample which contributes to the photoacoustic signal can be changed by varying the modulation frequency. That is, when the modulation frequency is raised, the thermal diffusion length becomes short (representing the surface), and the signal intensity becomes weak. To the contrary, when the modulation frequency is lowered, the signal intensity becomes larger because of the contribution from depth. In the case of an ordinary Michelson interferometer, the modulation frequency (f) is expressed as $f = 2V\nu$, which depends on the mirror speed V (cm/s) and wavenumber ν (cm^{-1}). Therefore, the lower the mirror speed, the longer becomes the thermal diffusion length, i.e., greater penetration, so that the photoacoustic signal becomes larger. In Fig. 1, a substrate of 0.5 mm polycarbonate (PC) coated with a 5 μm layer of urethane polymer was measured at a mirror speed of 2 mm/sec. The result of measuring this sample at various mirror speeds is shown in Fig. 2, in which (a) shows the mirror speed of 2 mm/sec on the PC substrate, and (b), (c), (d) are the cases of mirror speed of 2, 4, 6 mm/sec from the coating surface, respectively. The faster the mirror speed, the smaller become the peaks (indicated by arrows) from the PC lower layer. Thus, by varying the mirror speed, depth profile spectra from several to tens of micrometers can be acquired.

following: 1. Most samples can be directly measured without treatment regardless of the state and shape, 2. Samples with poor optical characteristics of transmission or reflection can be measured, 3. The sensitivity of measurement is enhanced when the intensity of the light source is increased, and 4. Depthwise (μm scale) information can be obtained simply by varying the interferometer mirror speed. Shown here are examples of measuring high polymer pellet and powder materials using FTIR-PAS. Examples of measurement using several samples are shown here to illustrate these features.

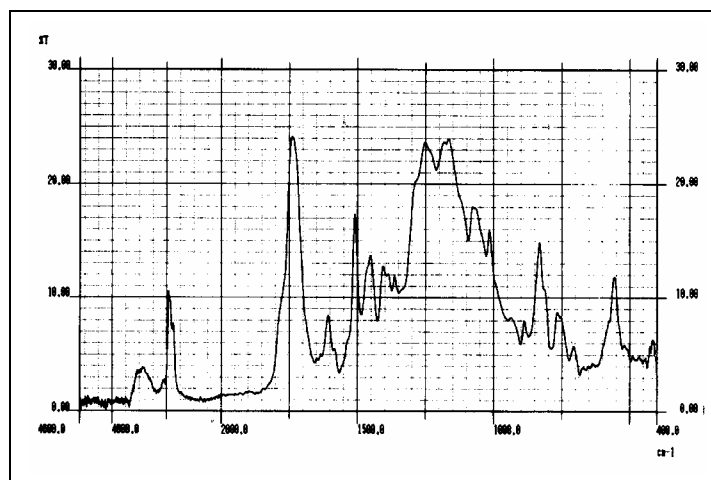


Fig. 1 Photoacoustic Spectrum of Coated Polycarbonate Plate

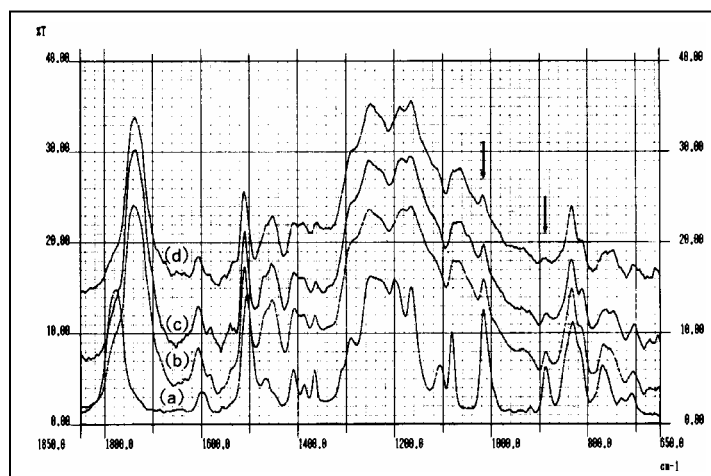


Fig. 2 Photoacoustic Spectra with Different Mirror Speed

Table 1 Analytical Conditions

Resolution : 8 cm^{-1}
Accumulation : 500 (1000 for (d))
Apodization : Happ-Genzel
Purge Gas : He

Analysis of Coatings (paint film)

Infrared spectra of coat films are normally measured using the ATR method, normal reflectivity method and high sensitivity reflectivity method, and the appropriate one of these must be selected depending on the film thickness of the sample, and/or type of substrate. On the other hand, PAS is capable of accepting any sample regardless of its condition. Fig. 3 shows the photoacoustic spectra of the outside (a) and inside (b) of a beverage can. Fig. 4 shows the with PAS, a wide variety

photoacoustic spectrum of a paint coated on wood. Thus, of coatings can be easily measured.

Table 2 Analytical Conditions

Resolution : 8 cm ⁻¹
Accumulation : 500
Apodization : Happ-Genzel
Mirror Speed : 2.0 mm/sec
Purge Gas : He

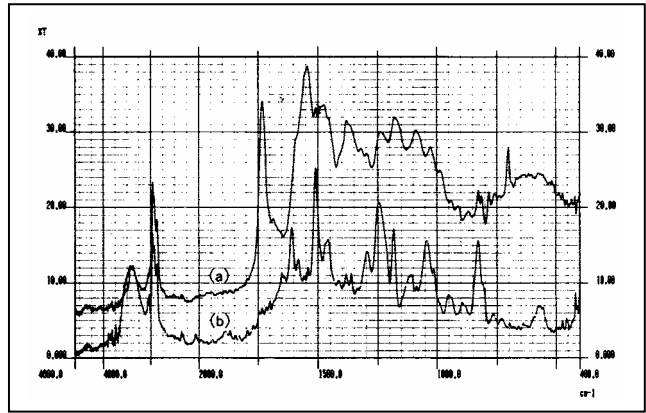


Fig. 3 Photoacoustic Spectra of Outside (a) and Inside (b) of Beverage Can

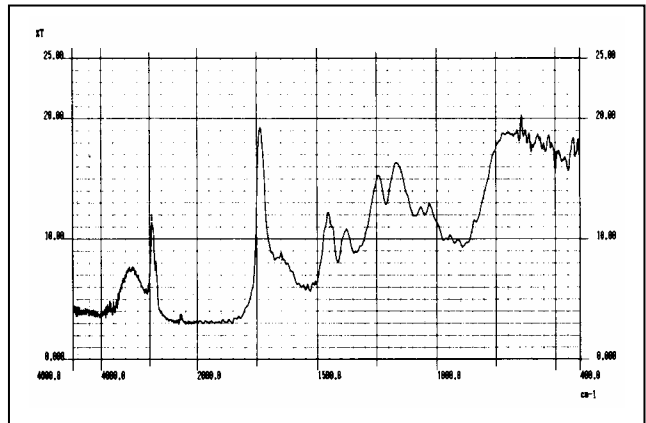


Fig. 4 Photoacoustic Spectrum of Paint Coated on Wood

Analysis of Hair

To measure the infrared spectrum of hair, the ATR method and infrared microscope method are known, but the PAS is the best method for simply measuring a portion of only one hair. This is to show the result of measuring a hair coated with a commercial conditioner for preventing the splitting of hair. Fig. 5 (a) shows the spectrum of a coated hair, and (b) is the photoacoustic spectrum of the same hair uncoated. Fig. 6 shows the difference spectrum

of (a) - (b). Near 1260, 1100 and 800 cm⁻¹, there are absorption bands of the high polymer silicone which is the active agent in this particular conditioner.

Table 3 Analytical Conditions

Resolution : 8 cm ⁻¹
Accumulation : 500
Apodization : Happ-Genzel
Mirror Speed : 2.0 mm/sec

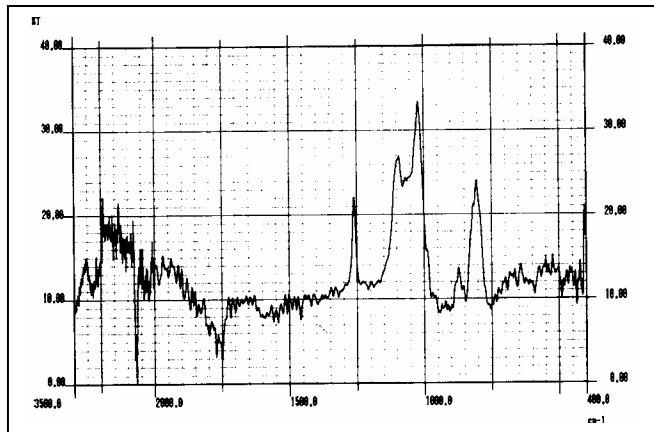


Fig. 5 Photoacoustic Spectra of Coated (a) and Uncoated (b) Hair

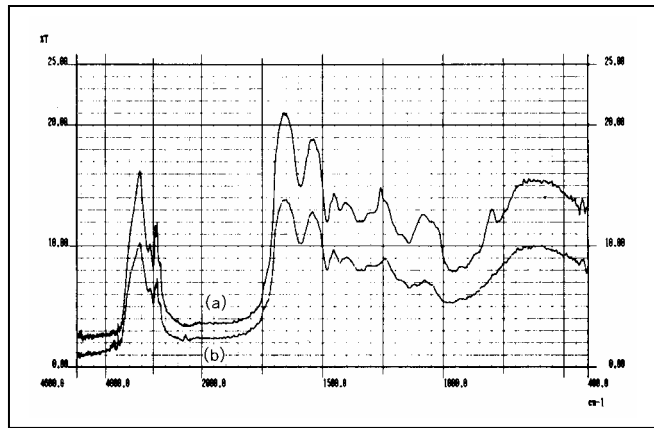


Fig 6 Difference Spectrum