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PHOTO-ACOUSTIC SPECTROSCOPY OF SYNTHETIC POLYMERS

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INTRODUCTION

Infrared spectroscopy has for many years been a preferred technique for the qualitative identification of synthetic polymers (Ref 1). The increased analytical precision of the instruments which are now available commercially has led to a considerable increase in the use of IR methods in quantitative analysis. This is particularly the case in the polymer field where conventional chemical methods are often not readily applicable eg in the quantitative determination of the composition of copolymers.

It is usual to measure IR spectra by transmission. Thus, when examining polymers it has been necessary in most cases to prepare the sample as a thin film, usually below 100µm in thickness. For a good quality spectrum, and certainly for satisfactory quantitative analysis, this film must be of uniform thickness.

It would be a great convenience to be able to measure spectra on polymer samples as received, without resorting to film preparation. Vidrine (Ref 2) has pointed out that if instead of measuring spectra by transmission they are measured by the photo-acoustic technique, it is possible to obtain good quality qualitative data from bulk solids, and, in the case of polymers, from powders, pellets or sheets.

We have extended these measurements to the examination of a polymer coating on a metallic substrate, and, to throw some light on the effect of sample dimensions on the quality of the photo-acoustic spectrum, we have compared the spectra of a series of polyester films of different thickness.

Finally, we offer some preliminary observations on quantitative analyses of copolymer in the mid infrared by the PAS technique.

Experimental

It appears that in the present state of development of the photo acoustic technique in the mid IR region, the sensitivity necessary to record a useful spectrum can only be obtained on a reasonable time scale by the use of Fourier transform spectrometers (PAFTIR). All our spectra were measured with the photo-acoustic cell type OAS401 from EDT Research, UK. The cell was fitted with a potassium bromide window for this mid IR study. The spectrometer used was the Nicolet 7199 (Nicolet Instruments Corporation USA). The mechanical and electric interfacing and the general experimental procedure is as described by J M Chalmers et al (Ref 3).

RESULTS AND DISCUSSIONS

The validity of our experimental arrangement was confirmed by measuring the PAFTIR spectrum of polyvinyl chloride powder with our system and comparing this with the conventional transmission spectrum. The qualitative similarity was excellent, and, as was anticipated, the bands in the PAS spectrum showed a relatively greater intensity at lower frequency as compared with the transmission spectrum (Ref 3). This is a consequence of the form of modulation of the radiation which is inherent in the use of this type of FTIR instrument (Ref 4).

It is often useful to measure the spectrum of the polymer used as a coating on a metallic substrate. Figure 1b is the PAFTIR spectrum of a black polymer coating measured in situ on an aluminium container. In this instance, it was possible to dissolve the 3mm aluminium backing from the sample by immersion in concentrated sodium hydroxide solution leaving only the polymer layer, and the conventional transmission spectrum of this layer is shown in Fig 1a. Evidently heat transfer from this thin layer into a substantial metal backing does not significantly modify the PAFTIR spectrum. The general characteristics of both spectra show the coating to be based on polytetrafluoroethylene, but an additional band is evident at about 980cm^{-1}, showing the coating to be a copolymer of PTFE.

The result of the examination of a series of polyethylene terephthalate films is shown in Fig 2. The very thin film (±2.5µm) shows an extremely intense spectrum, with high contrast. When the film thickness is increased, to 9µm, and then to 100µm, the signal level decreases and also the signal contrast (ie difference in signal level between region of high and low absorption). It appears that the signal level stabilises after about 25µm, but with increasing sample thickness there is some improvement in contrast. Presumably this effect is due to heat transfer between the surface and interior of the sample. In very thin samples, heat cannot "soak away", but is immediately re-emitted from the surface, giving a high signal level. As the sample thickness increases heat is conducted away from the surface reducing the signal level, but is then re-emitted from the interior of the sample, reducing the contrast. Eventually when the thickness of the sample exceeds the "thermal penetration depth" the spectrum stabilises and becomes independent of sample thickness. Thus it appears that there is significant degradation of the PAFTIR spectrum with increasing thickness, although the spectrum remains recognisable even at "infinite" thickness. This is in contrast to the emission spectrum, where, with increasing sample thickness the spectrum eventually becomes almost unrecognisable as an absorption spectrum.

Finally, we have examined the PAFTIR spectra of a series of vinyl chloride/vinyl acetate copolymers in powder form (Ref 3). Perhaps surprisingly, the spectrum appeared to be little influenced by change in particle size from below 50µm to upwards of 200µm (Ref 5). Examination of these spectra suggests that a number of the bands could be used for a quantitative determination of copolymer proportions.

For example, the bands at ≈1430cm^{-1} (-CH$_2$- group) and at ≈1378cm^{-1} (-CH$_3$ group) may be selected. A plot of

$$\frac{\text{signal at } 1378\text{cm}^{-1}}{\text{signal at } 1430\text{cm}^{-1}}$$

versus acetate content is found to be approximately linear. There seems good reason to believe that quantitative analysis should be possible when spectra are measured by the photo-acoustic technique.

REFERENCES

1 D Hummel, Kunotstoff, - Lack - and Gummi - Analyse, Carl Hanser, Munchen 1958

2 D W Vidrine, Applied Spectroscopy 34, 314 (1980)

3 J M Chalmers, B J Stay, G F Kirkbright, D E M Spillane and B C Beadle. Accepted for publication by The Analyst

4 R E Blank and T Wakefield, Anal Chem 51, 50, (1979)

5 D E M Spillane and G F Kirkbright. Paper to be read at this meeting.

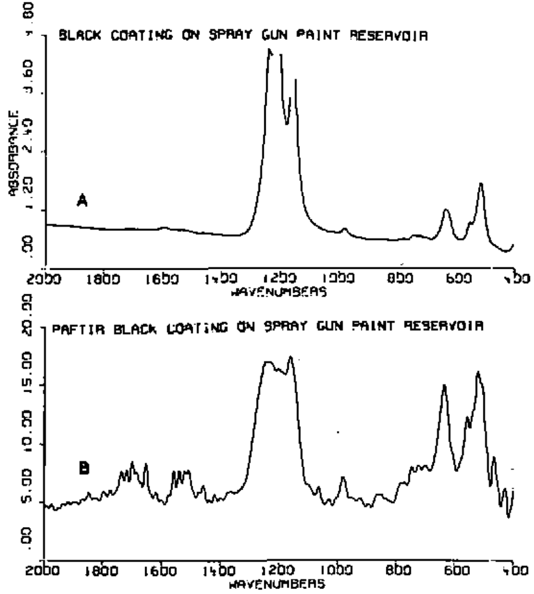

Fig 1. Spectra of polymer coating on metal surface.

(A) Transmission spectrum of coating removed from metal Surface.

(B) PAFTIR spectrum of coating on metal surface in situ.

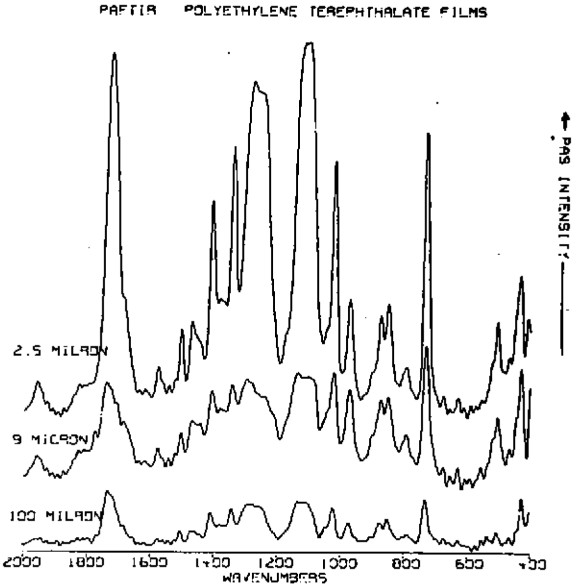

Fig 2. PAFTIR spectra of polyester films of different thicknesses.