Depth profiling of multi-layer polymer systems using *FT*i.r. phase analysis photoacoustic spectroscopy

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Polydimethylsiloxane spin-coated onto a thermosetting acrylic copolymer substrate was used as a test sample to investigate the use of Fourier transform infra-red phase analysis photoacoustic spectroscopy *FT*i.r.PAPS. *FT*i.r.PAPS spectra derived from the imaginary component of the uncorrected interferogram are shown to be more bulk sensitive than the corresponding spectra derived from the real component. Furthermore, data obtained by this method can be shown to suffer less from photoacoustic saturation and, therefore, quantitative results are better. Depending on the thermal properties of the material to be examined this method offers improved depth of penetration or improved depth resolution of the substrate under investigation.

(Keywords: Fourier transform infra-red spectroscopy; multi-layer polymer system; photoacoustic spectroscopy)

INTRODUCTION

The separation of surface and bulk absorption coefficients in photoacoustic spectroscopy was dealt with theoretically by Bennett and Forman[1]. More recently, using phase analysis, improved depth resolution and the elimination of saturation effects have been reported by Bertrand *et al.*[2,3] studying the sorption of water in polyethylene. The conventional method of depth profiling using Fourier transform infra-red photoacoustic spectroscopy (*FT*i.r.PAS), which has been successfully applied to multilayer systems by Urban[4], relies on the relationship which exists between the first thermal diffusion length (μ) and the modulation frequency (f)

$$\mu = (2\alpha/f)^{1/2} \tag{1}$$

where $f = 4\pi V\nu$ (with V = mirror velocity (cm s^{-1}) and ν = wavenumber (cm^{-1}) and $\alpha = K/\rho c$ is thermal diffusivity (with K = thermal conductivity, ρ = density and c = specific heat). In accordance with equation (1), a decrease in modulation frequency causes an increase in thermal diffusion length and, therefore, the photoacoustic signal that reaches the surface comes from a greater depth. Thus, by altering the mirror velocity of the interferometer, the modulation frequency can be varied and hence depth profiling accomplished.

A problem with quantifying data obtained in this way is that the photoacoustic signal does not scale linearly with absorption coefficient for highly absorbing systems. Thus the signal can be observed to saturate for materials with large absorption coefficients or similarly for large penetration depths. Either extreme or a combination of both factors will result in saturation.

It has been shown that the use of phase analysis can alleviate the above problem. The signal derived from the quadrature component has been shown to be linear with absorption coefficient over a much larger range and hence saturation is not likely to be experienced for spectra obtained using this part of the phase[3]. Also, the conventional method of depth profiling is limited in resolution by the number of discrete mirror velocities achievable with a given interferometer. Furthermore, the depth of penetration is limited by modulation frequency, which is related to the mirror velocity, as well as by the thermal properties of the material.

In this work, we will show that it is possible to obtain spectra which represent different depths, using the same mirror velocity, by comparing spectra obtained from the sine and cosine transforms of the interferogram. One of the transforms, cosine or imaginary, can be shown to be less subject to photoacoustic saturation and therefore more suitable for quantitative interpretation.

EXPERIMENTAL

Hydroxy-tipped polydimethylsiloxane (PDMS), supplied by Rhone Poulenc, was spin-coated from a xylene solution onto a thermosetting acrylic copolymer consisting of poly(methylmethacrylate-*co*-glycidylmethacrylate) (MMA/GMA). The PDMS layer was 5–10 μm thick on a 50 μm thick acrylic substrate. A photoacoustic attachment (MTEC 100) was used with a Mattson Cygnus 100 *FT*i.r. spectrometer. The spectra were recorded using highly oriented stress annealed pyrolytic graphite as a reference sample. This material was chosen because of its highly crystalline layered structure, which makes it ideally suited since the original photoacoustic theories are derived using a model which relies on this type of structure[5]. Six mirror velocities were used: 0.08, 0.12, 0.18, 0.32, 0.62 and 1.27 cm s^{-1}. The higher mirror velocities available could not be used due to unacceptable signal to noise ratio. All spectra were recorded using a resolution of 4 cm^{-1}.

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RESULTS

Photoacoustic spectra recorded at a mirror velocity of 0.12 cm s^{-1} for the two components PDMS and MMA/GMA acrylic copolymer are shown in *Figure 1*. We can identify two bands for which there is no significant overlap: at 785 cm^{-1} (–CH_3 rocking mode) for PDMS and 1718 cm^{-1} (carbonyl stretching) for the acrylic. The ratio of these two bands can be used to give the percentage composition as a function of depth.

Figure 2 shows spectra obtained for the sample prepared as described above. The spectra are shown for six different mirror velocities or six different volume elements which vary in depth in a direction normal to the surface. The depth is given by the first thermal diffusion length for the particular materials. For the acrylic, values of thermal conductivity $K = 0.193$ W m^{-1} K^{-1}, density = 0.973 g cm^{-3} and specific heat $c = 1.55$ kJ kg^{-1} K^{-1} were used. Using these values in equation (1), the sampling depth given by the first thermal diffusion length (μ) was calculated for each mirror velocity at both 3000 and 500 cm^{-1}. It can be seen from the values reported in *Table 1* that for a mirror velocity of 0.08 cm s^{-1} the spectrum should sample both the top PDMS layer (5–10 μm thick) and the acrylic substrate (50 μm thick). This is shown by the appearance of both PDMS and acrylic bands in the spectrum. The acrylic bands at 2930, 1720, 1430 and 1130 cm^{-1} are all observed to decrease in intensity with increasing mirror velocity, as predicted from the estimated sampling depths shown in *Table 1*. Note that the decrease in intensity of the carbonyl band with increasing mirror velocity is not as consistent when carbon black is used as a reference material.

For $V = 1.27$ cm s^{-1} only the most intense C–O–C stretching vibration (acrylic) is detectable at 1130 cm^{-1} as the sampling depth is only slightly greater than the thickness of the PDMS layer for $\nu = 1130$ cm^{-1}. Similarly, the carbonyl band at 1720 cm^{-1} is barely visible, which is consistent with the estimated thickness of the PDMS layer and the penetration depth at 1720 cm^{-1} for $V = 1.27$ cm s^{-1}. Unfortunately, any attempt to use the ratio of an acrylic band to a PDMS band to estimate composition for a given depth must take into account three factors: the variation in penetration depth with wavelength; the variation of signal to noise ratio with mirror velocity; and photoacoustic saturation. These

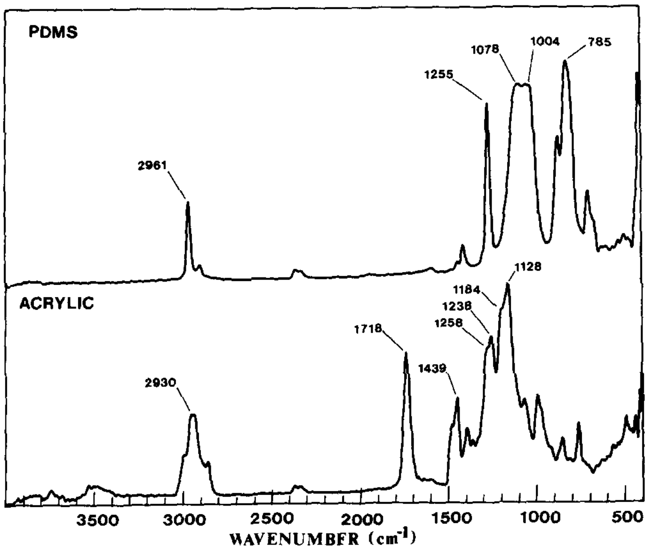

Figure 1 Photoacoustic *FT*i.r. spectra at mirror velocity = 0.12 cm s^{-1} for a 50 μm layer of PDMS cured with tetraethyl-ortho-silicate on an aluminium substrate and 50 μm MMA/GMA cured with dodecanedioic acid at 170°C on an aluminium substrate

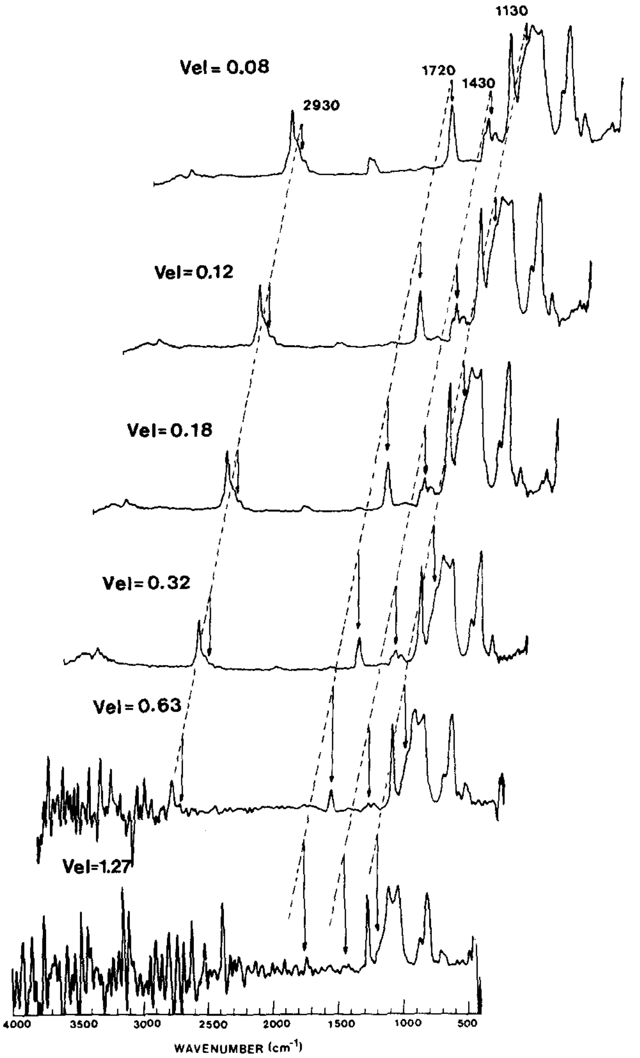

Figure 2 Photoacoustic *FT*i.r. spectra taken over a range of mirror velocities for a multilayer sample consisting of a layer of PDMS (10 μm) spin coated onto a layer of a MMA/GMA acrylic copolymer on an aluminium substrate

Table 1

Mirror velocity (cm s^{-1})	Wavenumber (cm^{-1})	Thermal diffusion length μ (μm)	
		Acrylic	PDMS
0.08	3000	8.7	29.7
	500	21.4	72.8
0.12	3000	7.1	24.2
	500	17.5	59.3
0.18	3000	5.8	19.8
	500	14.2	48.3
0.32	3000	4.36	14.8
	500	10.6	36.3
0.63	3000	3.1	10.5
	500	7.6	25.8
1.27	3000	2.2	7.4
	500	5.4	18.2

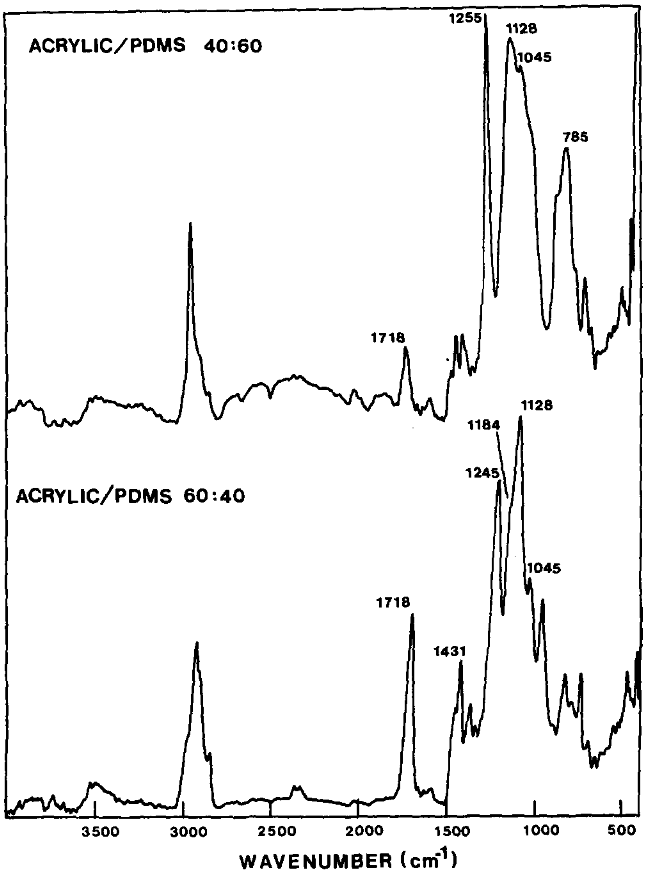

Figure 3 Spectra produced by the digital addition of the PDMS and acrylic spectra shown in *Figure 1*

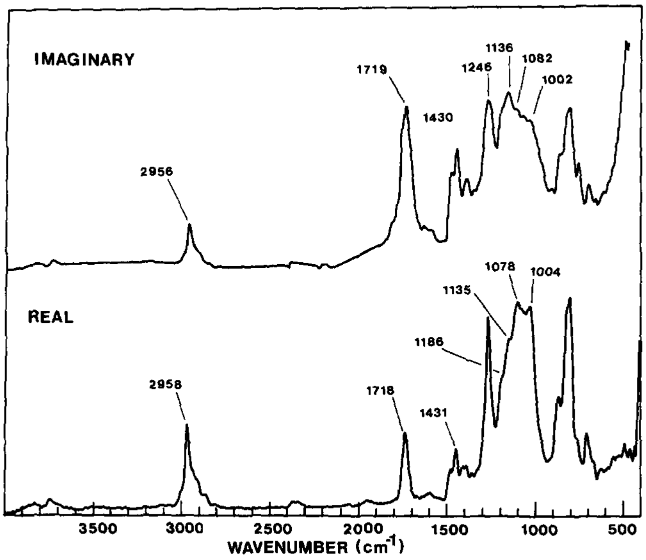

Figure 4 Photoacoustic *FT*i.r. spectra at mirror velocity = 0.12 cm s^{-1} obtained by analysis of the real and imaginary parts of the uncorrected interferogram for a PDMS/acrylic/Al multilayer sample

effects can best be seen if we compare spectra shown in *Figure 2* with spectra produced by the digital addition of the two component spectra.

Spectra for 40:60 and 60:40 ratios of acrylic:PDMS are shown in *Figure 3*. These obviously cannot take into account the changes in a spectrum due to the physical and chemical interaction of the two components, but they do serve as approximate guidelines for the expected ratio of the carbonyl (≈ 1720 cm^{-1}) and $-CH_3$ (≈ 785 cm^{-1}) bands for a given composition. We can see by comparing *Figures 2* and *3* that the higher the wavenumber and the higher the mirror velocity, the more severe is the reduction in intensity of a given band due to the aforementioned factors. Therefore, any attempt to calculate the ratio of the carbonyl band for the acrylic to the CH_3 band for PDMS, at a given mirror velocity, will give a value lower than the real value. Furthermore, any attempt to compare ratios for different mirror velocities to obtain relative values will also lead to error.

Figures 4 and *5* show spectra obtained from the sine and cosine transforms at mirror velocities $V = 0.12$ and 0.63 cm s^{-1}, respectively. If we again use the 1720 and 785 cm^{-1} bands as diagnostic for the acrylic and PDMS, respectively, it becomes apparent that the imaginary component is more bulk sensitive. This is the case for both mirror velocities. Acrylic/PDMS compositions determined from the ratios of the areas under the 1720 and 785 cm^{-1} bands in the imaginary spectra compare more favourably with those estimated by calculation from the depth sampled, for the respective mirror velocities, than compositions determined from the real component spectra. This can be explained by the fact that the imaginary spectra suffer less from photoacoustic saturation than the real spectra[3]. A detailed theoretical account will be given later[6].

CONCLUSION

The use of phase analysis has been shown to give better quantitative results than the conventional method of depth profiling. The use of phase analysis with a PDMS/acrylic sample has been shown to improve the depth of penetration. Using other samples with different thermal properties, one might expect to observe either improved depth of penetration or improved depth resolution.

We have introduced the use of highly oriented stress annealed pyrolytic graphite as a reference material for

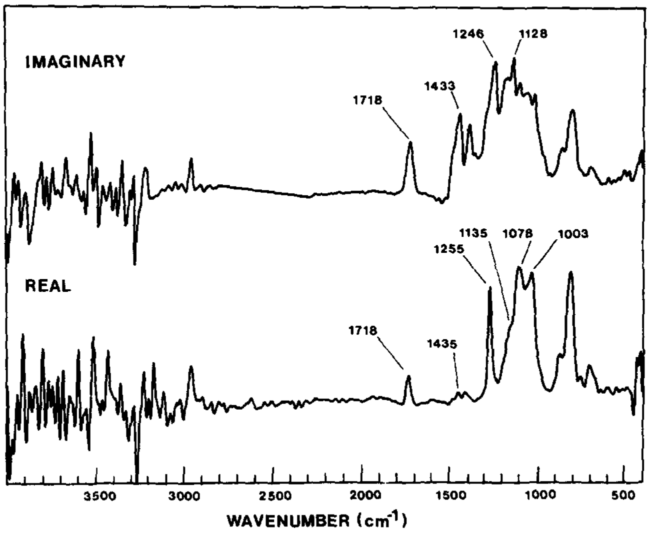

Figure 5 Photoacoustic *FT*i.r. spectra at mirror velocity = 0.63 cm s^{-1} obtained by analysis of the real and imaginary parts of the uncorrected interferogram for a PDMS/acrylic/Al multilayer sample

depth profiling. Variation in the depth of penetration with mirror velocity is reported to be more consistent if stress annealed pyrolytic graphite is used rather than the conventional carbon black as, based on photoacoustic theory, the layered structure of the former is more appropriate.

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