

Characterization of Polymer Laminates by Time-Resolved Step-Scan FT-IR Photoacoustic Spectroscopy (TR-S²FT-IR PAS)

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Abstract

Applications of time-resolved step-scan FT-IR photoacoustic spectroscopy (TR-S²FT-IR PAS) to qualitative and quantitative depth profiling of a polymer laminate are demonstrated. The experimental results confirm the relationship between frequency-domain and time-domain step-scan FT-IR as suggested by classic step-scan FT-IR theory: $\Delta\Phi = \omega \Delta t$.

Introduction

Frequency-domain phase modulation step-scan FT-IR has been traditionally used in the photoacoustic spectral (PAS) depth profiling analysis of polymer laminates, as seen from extensive work of the last few years.¹⁻⁵ The time-domain, non-phase modulation mode of step-scan FT-IR, on the other hand, has been used mostly in studying reversible fast chemical reactions. The combination of step-scan time-resolved spectroscopy (TRS) and photoacoustic spectroscopy has only been reported a few times for laminated sample analysis.⁴⁻⁶ This paper illustrates the capability of step-scan TRS for both qualitative and quantitative photoacoustic depth profiling of polymer laminates. A quantitative model for thickness determination of laminates based on the time-resolved step-scan FT-IR PAS data is demonstrated and experimentally confirmed.

Experimental

A Nicolet Nexus 870 step-scan spectrometer with an MTEC 300 photoacoustic cell was used to collect all time-resolved PAS data. The moving mirror stepping at a frequency of 3.8 Hz was used to generate "translation" modulation of the IR light and thus the photoacoustic signal. After minimum mirror settling time (1ms), the spectrometer sends out a trigger signal to initiate time-resolved data sampling for 100 ms. Figure 1 indicates the timing details of

mirror stepping, settling time, spectrometer triggering and time-resolved PAS sampling. The actual data collection parameters are easily set using the standard software. A Kapton™ film sample consisting of a sandwich of 12 μm of Teflon™ on 25 μm of polyimide on another 12 μm of Teflon™ was used in the experiment to demonstrate step-scan TR-PAS capabilities in depth profiling. In addition, two carbon black samples, carbon-black filled rubber and MTEC classy carbon reference, were also studied by TR PAS.

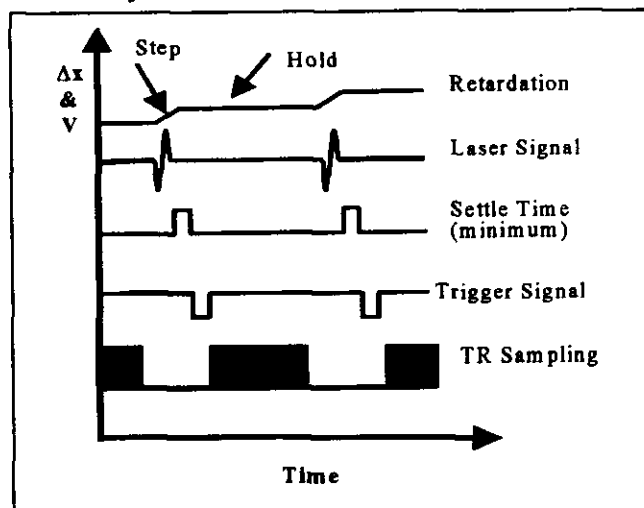


Figure 1. Nexus 870 S²TR-PAS timing and sampling scheme illustrates mirror stepping, mirror settling, and spectrometer triggering.

Results and Discussion

Time-resolved intensity profiles of the carbon black-filled rubber and the MTEC glassy carbon reference are illustrated in

Fig. 2. The data show that the glassy carbon reaches a maximum about 5 ms earlier than the carbon black-filled rubber. This indicates that the glassy carbon reference is a better "phase" or "surface" reference than the rubber, even though the rubber has a more intense amplitude spectrum. For both carbon samples, the PA signal reaches its maximum at a later time ($t = 23 \sim 28$ ms) rather than right at the beginning ($t = 0$) of mirror translation modulation, indicating relatively slow thermal (acoustic) response to IR modulation.

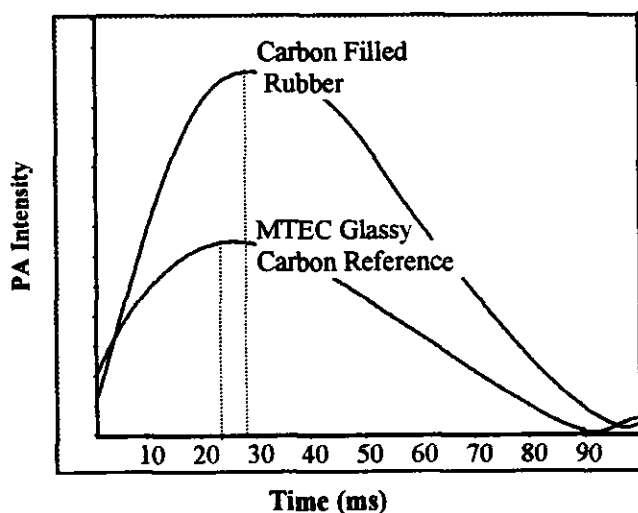


Figure 2. Step-scan time-resolved photoacoustic intensity profiles of carbon black filled rubber and the standard MTEC glassy carbon reference, over total sampling time of 100 ms for each mirror step.

The step-scan TR-PA spectra of the Kapton™ sample are shown in Figure 3. The spectrum at 13 ms clearly has relatively strong Teflon bands at 1264 and 1172 cm^{-1} whereas, these two bands are considerably reduced in relative intensity at 50 ms. The relative intensities of the sub-layer (polyimide) bands, 1716 and 1600 cm^{-1} , on contrary, increase at 50 ms.

The time-resolved intensity profiles of this sample are demonstrated in Figure 4. We can see in Figure 4 that the surface Teflon bands, 1264 cm^{-1} and 1172 cm^{-1} , reach their maximums at about the same

time, 43 ms, since their intensities are about the same, whereas the polyimide bands, 1716 cm^{-1} and 1600 cm^{-1} reach their maximums at relatively later times, 49 and 50 ms respectively. The 1 ms delay for the band 1600 cm^{-1} to reach maximum is due to its weaker intensity, suggesting more contribution from the deeper part of polyimide layer. These results clearly distinguish the spatial origins of the Teflon and polyimide bands.

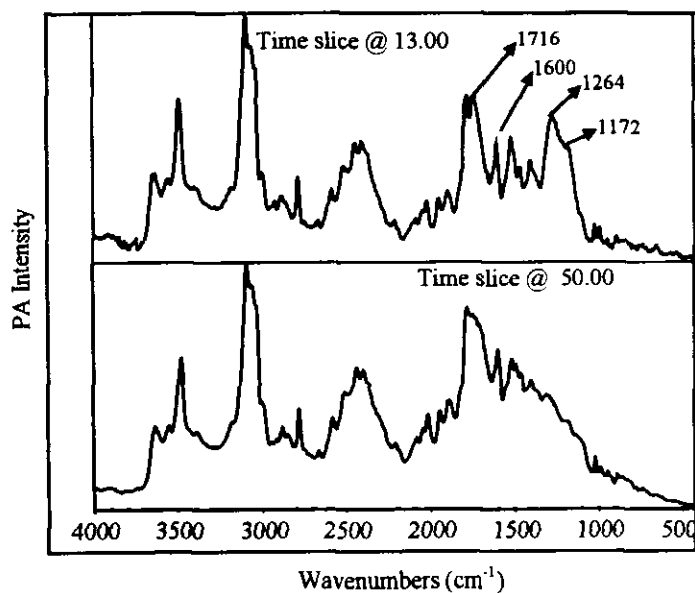


Figure 3. Time-resolved step-scan PA spectra of Kapton™ film at 13 and 50 ms respectively.

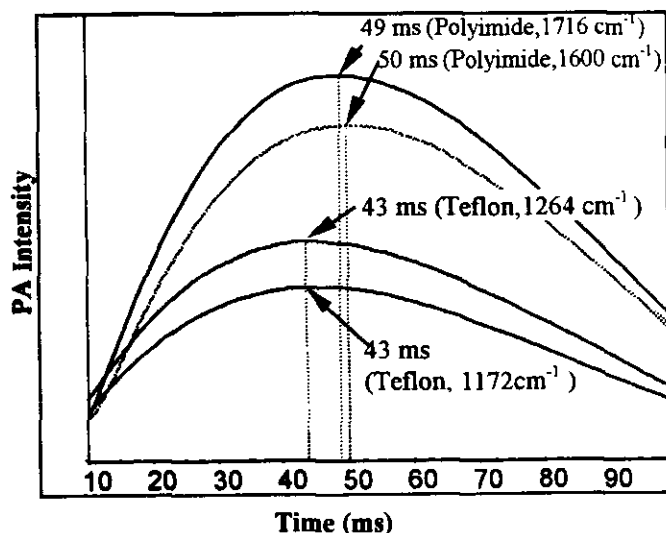


Figure 4. Time-resolved intensity profiles of Teflon and polyamide bands.

As was discussed extensively in previously published work¹⁻² dealing with step-scan phase resolved PAS, the thickness (d) of top layer can be conveniently calculated from the phase difference ($\Delta\Phi$) between two strong bands of the surface and the substrate by $d = \Delta\Phi \mu$, where μ is the thermal diffusion depth at the phase modulation frequency. The time-domain (time-resolved) results can be conveniently related to frequency-domain (phase resolved) results by

$$\Delta\Phi = \omega \Delta t \quad (1)$$

where $\omega = 2 \pi f$, f is modulation frequency, and Δt is time difference. Thus in TR-S²PAS,

$$d = \Delta\Phi \mu = (2 \pi f) \Delta t * \mu \quad (2).$$

Therefore the thickness of the top TeflonTM layer can be calculated by using equation (2) with $f = 3.8$ Hz, $\Delta t = 49-43 = 6$ ms = 0.006 s, $\alpha = 0.001$ cm²/sec, $\mu = (\alpha/\pi f)^{1/2} = [(0.001 \text{ cm}^2/\text{s})/3.14 \times 3.8 \text{ Hz}]^{1/2} = 92$ μm , i.e. $d = (2 \pi f) \Delta t * \mu = 2 \times 3.14 \times 3.8 \times 0.006 \times 92 = 13$ μm . This is very close to the actual thickness (12 μm) of the layer and also to the results determined by the phase-resolved method.⁷

Conclusions

Layered polymeric materials can be studied by step-scan FT-IR PAS in both time-domain and frequency-domain. Time-resolved step-scan FT-IR photoacoustic spectroscopy (TR-S²FT-IR PAS) provides a very intuitive method for both qualitative and quantitative depth profiling studies of laminates. The results from TR-S²FT-IR PAS are in consistent with the phase-resolved step-scan FT-IR PAS.⁷ Practical depth profiling applications of TR-S²FT-IR PAS based on the simple stepping modulation setup is highly suggested.

References

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Note:

TeflonTM and KaptonTM are trade marks of E. I. DuPont de Nemours and Company.