A Polymer Double-layer Studied by Step-scan FTIR Photoacoustic Spectroscopy

M.W.C. Wahls[1,*] and J.C. Leyte[1], J.M.F. Swart[2] and P.C.M. van Woerkom[2]

1) Leiden Institute of Chemisty, Gorleaus Laboratories,
Physical and Macromolecular Chemistry, Leiden University,
P.O. Box 9502, NL-2300 RA Leiden, the Netherlands
2) Akzo-Nobel Central Research, P.O. Box 9300,
NL-6800 SB Arnhem, the Netherlands

Abstract: Photoacoustic (PA) magnitude and phase spectra of a polyethylene/polyurethane double-layer are presented. The extension of the Rosencwaig-Gersho theory to a double-layered polymer film introduced by N.C. Fernelius in 1980 is applied to compare the experimental spectra with simulations. A reasonable agreement between experiment and simulation is observed. It is shown that FTIR-PAS in combination with simulation provides an important technique for depth profiling in polymeric laminates.

Introduction

Step-scan FTIR photoacoustic spectroscopy [PAS] can be applied for depth profile studies in polymeric laminates. PAS is depth-sensitive in the sense that the thermal waves corresponding to individual IR-bands may originate at different depths in the sample. In 1976, Rosencwaig and Gersho[1] were the first to present a complete theory for the photoacoustic effect. They solved the thermal diffusion equation of the heat caused by the absorption of modulated infrared light. The so-called RG-theory relates the photoacoustic response with signal magnitude [Mag] and signal phase [ϕ] to the optical absorptivity [β] and thermal conductivity [κ] of the investigated homogeneous layer with thickness [l]. The extension of the RG-theory to double-layered polymer

 CCC 1022-1360/99/$ 17.50+.50/0

films, which are attached to a thermal conductor (e.g. a metal backing), was introduced by Mandelis et al.[2] and by Fernelius [3,4] in 1980.

Since step-scan interferometers became available around 1990, numerous PA phase studies of layered polymer films have been published. Mostly, they present calculated phase differences between the maxima of IR-PA bands of individual layers. These phase-shifts may be used to calculate a layer thickness in multi-layered structures. They can also be applied to assign IR-PA bands to an individual layer in a laminate. In 1995, Jiang et al.[5] presented a phase-difference approach to calculate contributions from different layers of a polymer multi-layer. They introduced expressions for PA signal phase differences for various limits of the RG–theory, i.e. optically transparent or opaque polymer films, which are either thermally thin or thick.

Recently, we presented simulated and experimental PA phases and magnitudes of polymeric double-layers[6]. The full solution, i.e. Fernelius' expression, describing the photoacoustic effect was applied to compare experimental PA-magnitudes and phases to simulated data. It turned out, that only the use of the full description of the PA effect provides a clear understanding of the PA phase data of polymeric double-layers. This work extends a paper by Dubois et al.[7] from 1994, where experimental PA intensities are used to determine the optical absorption coefficient. We have presented also a PA study of a model polymer-coating system[8], i.e. a double-layered polymer film, which was attached to various metal substrates. An influence of the thermal characteristics of the backing on the photoacoustic signal of the coating was found. A correlation of PA-phases and mechanical adhesion strength of the interface should be expected. If this is confirmed, PA phase data may provide a new and non-destructive method to estimate a mechanical parameter, i.e. the adhesion strength.

Here, we present a photoacoustic study on a polymer bilayer. Experimental PA magnitude and phase spectra of the chemically heterogenous double layer polyethylene on polyurethane (PE / PU) are compared with the theory[3,4]. The necessary optical absorption coefficient β was obtained from the single-layer IR-transmission spectra. It turns out, that the experimental IR-PA spectra confirm the simulations. We found an increasing phase-shift between first- and second-layer absorptions in the

phase spectrum with an increasing phase modulation frequency. The overall range of the experimental phase spectrum exceeds $\pi/2$ and is observed as "backfolding" of phase peaks in the experimental phase spectrum at either the 45° or the 135° limit. A systematic deviation between experimental phases and the simulated data may indicate the existence of a thermal barrier at the interface of the polymer double layer.

Experimental set-up and simulation procedure

The PA spectra were collected by a Bio-Rad FTS 60A step-scan interferometer coupled with a MTEC 300 photoacoustic cell. Since in the step-scan mode a constant phase modulation is applied to all wavelengths of the IR-radiation, a constant thermal length μ is generated over the entire infrared spectral range.

μ is given as $(\kappa / \rho C_p \pi f)^{1/2}$, where κ is the thermal conductivity, ρ the density, C_p the heat capacity and f the modulation frequency. μ defines the length, where the thermal wave is damped out by a factor e^{-1} ($\cong$ 36.8 %), but a photoacoustic response may be observed from depths up to 5μ ($e^{-5} \cong 0.7$ %). The term "photoacoustic scanning depth" for μ should therefore be used with great care, since μ is not to be taken as the depth from which the signal originates. In the step-scan mode, the orthogonal symmetric in-phase and in-quadrature interferograms with respect to the optical phase modulation are simultaneously detected. The data are obtained with intervals of one wavelength of the reference He-Ne laser at a spectral resolution of 8 cm^{-1}. The chosen phase modulation frequencies are 50 and 400 Hz, respectively. The signals are demodulated by a two channel lock-in amplifier (Stanford SR 830 DSP), and returned to the FTS 60A for Fourier transformation. By Fourier transformation, the two so-called single beam spectra, i.e. in-phase [IN] and the in-quadrature [QU] single beams, are obtained. Fernelius[2,3] extended the RG-theory for a double-layered polymer film. The PA response of a double-layered polymeric laminate is determined by the optical absorptivities, the thermal conductivities and the layer thicknesses of both the surface (coating) and the substrate (bulk) layer of the laminate, and the thermal characteristics of the He-gas and the backing material.

The complex envelope Θ of the sinusoidal temperature variation for the double-layered polymer film is given by [2,3]:

$$\Theta\{(1-b)\exp(-\sigma_s l)[(1-c)(1+g/c)\exp(\sigma_c h)+(1+c)(1-g/c)\exp(-\sigma_c h)]-(1+b)\exp("+"\sigma_s l)$$
$$\times[(1+c)(1+g/c)\exp(\sigma_c h)+(1-c)(1-g/c)\exp(-\sigma_c h)]\}$$
$$=2E[2(r_s-b)\exp(-\beta l)+(1+b)(1-r_s)\exp(\sigma_s l)-(1-b)(1+r_s)\exp(-\sigma_s l)]$$
$$+Z[2(1-b)(1+r_c)\exp(-\sigma_s l-\beta_c h)-2(1+b)(1-r_s)\exp(-\sigma_s l-\beta_c h)-(1-b)(1-c)(1-r_c/c)$$
$$\times\exp(-\sigma_s l+\sigma_c h)-(1-b)(1+c)(1+r_c/c)\exp(-\sigma_s l-\sigma_c h)+(1+b)(1+c)(1-r_c/c)$$
$$\times\exp(\sigma_s l+\sigma_c h)+(1+b)(1-c)(1+r_c/c)\exp(\sigma_s l-\sigma_c h)] \qquad (1)$$

with $Z = \beta_c I_0 / [\, 2\kappa_c (\beta_c^2 - \sigma_c^2)]$, and $E = Z \exp(-\beta_c h)$. The solution Eq.(1) of the thermal diffusion equation[3,4] contains one correction; it is marked by one revised sign "+" within Eq.1: β_j = optical absorptivity; I_0 = incident monocromatic light flux; κ_j = thermal conductivity; l = intermediate layer thickness; h = surface layer thickness; a_j = thermal diffusion coefficient; $\sigma_j = (1+i)a_j$; $b = (\kappa_b\sigma_b / \kappa_s\sigma_s)$; $g = (\kappa_g\sigma_g / \kappa_s\sigma_s)$; $r_s = (1-i)\beta_s / 2a_s$; $c = (\kappa_c\sigma_c / \kappa_s\sigma_s)$; and $r_c = (1-i)\beta_c\kappa_c / 2a_s\kappa_s$. j can take g, c, s, or b. The surface layer (the coating) is denoted by subscript c, the substrate layer (the bulk) is denoted by subscript s, the He gas is denoted by subscript g, and the metal backing is denoted by subscript b. The pressure variation (the PAS signal) detected at the microphone is:

$$P(t) = Q \exp[i(\omega t - \pi/4)] \qquad (2)$$

with $Q = (\gamma P_0 / 2^{(1/2)} l_g T_0)*(\Theta / a_g)$.

We used this solution for the evaluation of the PA magnitude of the acoustic pressure variation in the cell caused by the PA effect. The PA magnitudes and phases are simulated with the full equations (1,2) being used. The necessary optical absorption coefficient β was obtained from an IR-transmission spectrum. The polymer film under investigation was not fixed on a (metal-) backing, thus the thermal characteristics of helium characterize the backing for each laminate. For reasons of simplification, we used identical values of κ, ρ, and C_p for both PE and PU:

κ = 5*e(-4) [cal/(cm s °C)], ρ = 0.92 [g/cm^3], and C_p = 0.55 [cal/(g °C)] [9]. A thermal diffusity α = 0.001 cm^2/sec is calculated. The simulated PA magnitude is obtained from the real (RE) and imaginary (IM) parts of [θ/a_g], as given by Mag = sqrt (RE^2 + IM^2). The signal magnitude equals the magnitude of [θ/a_g] up to factor, being constant in the usual experiments.

The experimental PA magnitude Mag_{PAS} and phase spectrum ϕ_{PAS} can be calculated from the in-phase and in-quadrature single beam spectra according to the equations (3a,3b):

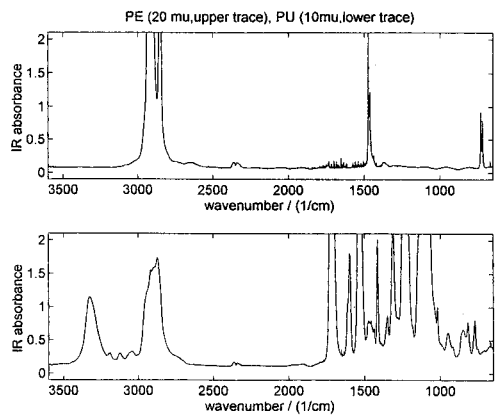
$$Mag_{PAS} = (IN^2 + QU^2)^{1/2} \quad (3a)$$

$$\phi_{PAS} = \tan^{-1}\left(\frac{QU}{IN}\right) \quad (3b)$$

Results and Discussion

Infrared-transmission spectra of the single-layered PE and PU films were measured and used to determine the optical absorption coefficient β as a function of the wavenumber. In figure (1), their single-layer IR absorbance spectra are shown for illustration.

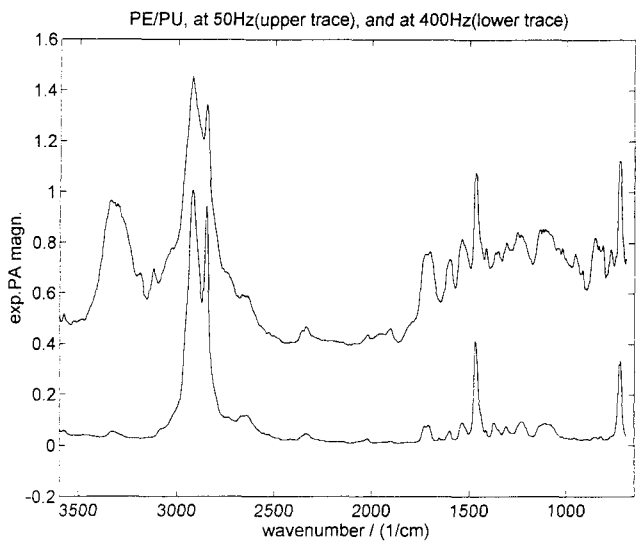
Fig. 1



The double-layered laminate is photoacoustically investigated at two phase modulation frequencies, i.e. 50 and 400 Hz. The PE-layer, of thickness 20 μm, was placed as the top-layer. Therefore, the PU-layer of thickness 10 μm, served as the substrate. By increasing the frequency from 50 Hz to 400 Hz, the thermal diffusion length μ is decreased from about 25 μm to approximately 8.5 μm. A depth profile containing spectral information of mainly the first (top) layer is expected for the 400 Hz measurement, while PA-spectra with spectral information of both layers should be obtained for the 50 Hz measurement.

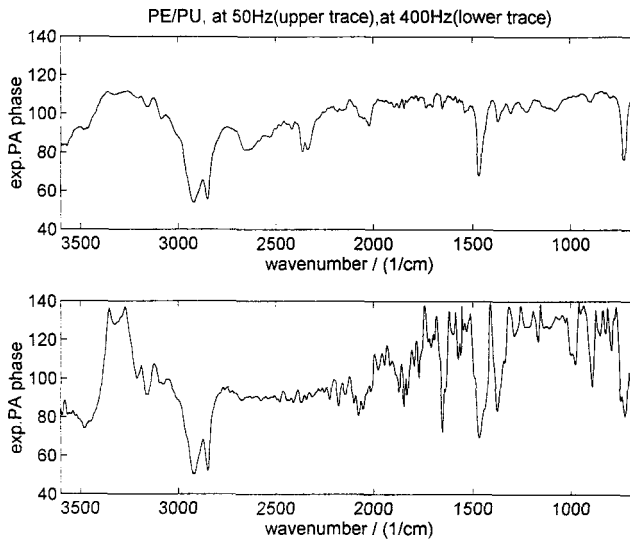
In figure (2), the normalized PA magnitude (acc. to Eq.(3a)) spectra at 50 and 400 Hz of the PE/PU double-layer are shown. At 400 Hz phase modulation, a PA magnitude spectrum is obtained, which contains mainly IR-bands of the PE surface-layer[10], i.e. 2920, 2850 cm^{-1} (CH stretch.), 1474 cm^{-1} (CH_2 deform.vibr.), and 731, 720 cm^{-1} (CH_2 rocking mode). The PA magnitude spectrum at 50 Hz phase modulation (with an offset in y-scale) however shows, as expected, many IR-bands of the PU-layer as well[10], i.e. 3325 cm^{-1} (NH vibr.), 1720 cm^{-1} (CO stretch.), 1600, 1530 cm^{-1} (PU-vibrations), 1415 cm^{-1} (CN stretch.), 1350 cm^{-1} (CH_3 sym.deform.) 1310, 1100 cm^{-1} (CH_2 skel.vibr).

Fig. 2



In figure (3), the experimental PA phase spectra are presented, which are calculated according to equation (3b). They are corrected for $\phi_{apparatus}$ [11,12]. Increasing the phase modulation results in an increasing phase-shift between first- and second-layer absorptions. The overall range of the experimental phase spectrum $\Delta\phi$ exceeds $\pi/2$ and is observed as "backfolding" of phase peaks in the phase spectrum at the 135°, e.g. for the NH band at 3325 cm^{-1} and the poly-urethane bands at 1530, 1415 cm^{-1}. The experimentally obtained phase spectrum is calculated from the IN and QU single-beam spectra. Therefore, since $\Delta\phi$ cannot exceed $\pi/2$, back-folding of experimental PA phase peaks occurs [6,11].

Fig. 3

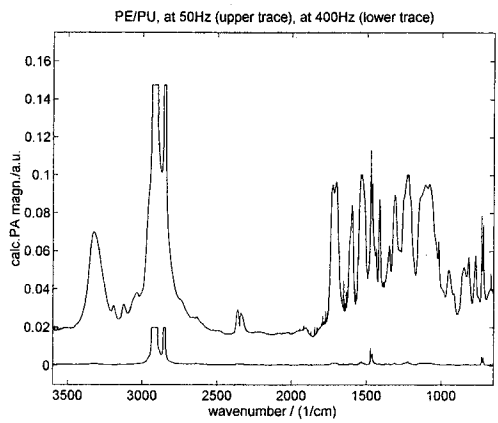


The very curious shape of the phase spectrum with the downward-pointing phase-peak of the CH stretching mode at 2900 cm^{-1} (of the PE) and the upward pointing phase-peak of the NH stretching mode at 3325 cm^{-1} (of the PU) was found experimentally. To check these experimentally obtained results, simulations were performed by using the Fernelius' expression for the PA signal, as given by equations (1,2).

In figure (4), the simulated PA magnitude spectra are shown for both 50 and 400 Hz phase modulation. The PA magnitude spectra indicate a dependency of the PA

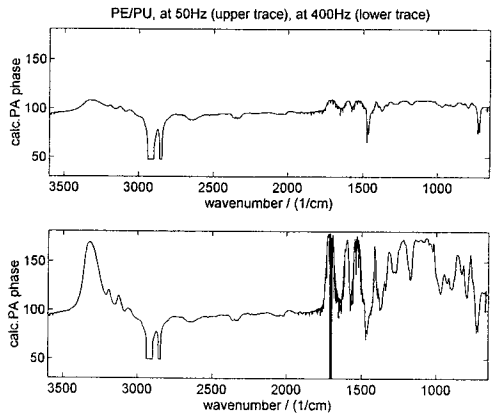
intensity on the phase modulation. The simulated PA magnitude spectrum at 400 Hz shows an approximately pure spectrum of the top-layer, i.e. the PE. At 50 Hz phase modulation however, IR-bands of both layers, i.e. PE and PU, are clearly observed. The experimental observation is therefore qualitatively confirmed.

Fig. 4



In figure (5), the simulated PA phase spectra at 50 and 400 Hz are shown.

Fig. 5



The simulated PA phase spectra confirm the experimental observations. The phase-peaks of the surface layer PE are determined between ≅ 50° and ≅ 70° with respect to the reference. The phase-peaks due to second layer absorptions are determined between ≅ 90°/100° to ≅ 180° with up-wards pointing phase-peaks as well.

It can be concluded, that the experimental observations for this polymeric double-layer are confirmed by simulated PA spectra. In particular, the curious shape of the experimentally obtained PA phase-spectrum with downward-pointing phase-peaks ("earlier phases") of first layer absorptions and upward-pointing phase peaks ("later phases") for second layer absorptions is clearly confirmed by the simulations. The systematic deviation between experimental and simulated PA phases, i.e. $\Delta\phi_{exp} < \Delta\phi_{calc}$ [as can be seen from Fig.(3) & Fig.(5)], may indicate a thermal barrier at the interface of the polymeric double-layer.

Conclusion

Experimental and simulated PA magnitude and phase spectra for a polymeric double-layer are compared. The simulation of PA spectra using Fernelius' expression for double layers was found to be very helpful for the interpretation of the experimental phase data in particular. It turned out, that the curious experimental observations in the phase spectra were confirmed successfully by the simulations.

No strict phase separation, i.e. $\pi/4$, between the single-layer IR absorptions occurs. This illustrates again, that the transport of modulated thermal waves caused by the absorption of IR radiation within the polymer double layer cause interdependent heat flows, as predicted by Rosencwaig & Gersho, and Fernelius. No strict phase shift seems to occur between individual layers of one laminate, in contrast with previous expectations[5].

References

[1] A.Rosencwaig, A.Gersho, J.Appl.Phys., 47, 64 (1976)

[2] A.Mandelis, Y.C.Teng, B.S.H.Royce, J.Appl.Phys., 50 (11), 7138 (1979)

[3] N.C.Fernelius, J.Opt.Soc.Am., 70 (5), 480 (1980)

[4] N.C.Fernelius, J.Appl.Phys., 51 (1), 650 (1980)

[5] E.Y.Jiang, R.A.Palmer, J.L.Chao, J.Appl.Phys. 78, 460 (1995)

[6] M.W.C.Wahls, J.C.Leyte, J.Appl.Phys. **83** (1), 504 (1998)

[7] M. Dubois, F. Enguehard, L. Bertrand, M. Choquet, and J.-P. Monchalin, J. de Physique **IV**, Colloque C7, C7-377 (1994)

[8] M.W.C.Wahls, J.C.Leyte, J. Appl. Spectros. **52** (1), 123 (1998)

[9] A.Rosencwaig, in Photoacoustics and Photoacoustic Spectroscopy, R.E. Krieger Publishing Company Inc., Malabar, Florida (1990)

[10] L.J.Bellamy, in: Advances in IR Group Frequencies, R.Clay (The Chancer Press) Ltd. Bunqay, Suffolk UK (1962)

[11] M.W.C.Wahls, J.P.Toutenhoofd, L.H.Leyte-Zuiderweg, J.de Bleijser, J.C.Leyte, J.Appl.Spectrosc. 51, 552 (1997)

[12] M.W.C. Wahls, J. L. Weisman, W. J. Jesse, and J. C. Leyte, *accepted for publication,* proceedings of the ICOFTS-11 Aug. 1997, Athens GA, USA