

## Comparative Study of Coating Thickness Determination in Packaging Composite Materials Using Photothermal Radiometry, Photoacoustic and Photopyroelectric methods

M. Chirtoc<sup>1</sup>, J. Gibkes<sup>2</sup>, H.G. Walther<sup>3</sup>, A. Christ<sup>4</sup>, J.S. Antoniw<sup>5</sup>, D. Bicanic<sup>6</sup>, Z. Bozoki<sup>7</sup>, G. Szabo<sup>7</sup>, B. Bein<sup>2</sup>, J. Pelzl<sup>2</sup>, M. Kleebauer<sup>8</sup>, H. Bader<sup>9</sup> and M. Marinelli<sup>10</sup>

<sup>1</sup>Lab. Acoustics and Thermophysics, Catholic Univ. Leuven, Belgium (On leave from INCDTIM, CP 700, 3400 Cluj-Napoca 5, Romania), <sup>2</sup>Ruhr-Univ. Bochum, Germany, <sup>3</sup>Inst. for Optics and Quantum Electronics, Jena, Germany, <sup>4</sup>Univ. Halle, Germany, <sup>5</sup>UFR Sciences, Reims, France, <sup>6</sup>WURC Univ. Wageningen, The Netherlands, <sup>7</sup>JATE Univ. Szeged, Hungary, <sup>8</sup>Papiertechnische Stiftung, Muenchen, Germany, <sup>9</sup>Hueck Folien GmbH, Germany, <sup>10</sup>Univ. Tor Vergata, Rome, Italy

Thickness measurements of transparent coatings on polymer, paper or metallic substrates used as packaging materials are reported. It is shown that thickness evaluations in the range between 1 and 75 μm are feasible by contact photothermal techniques (photoacoustics (PA), photopyroelectric (PPE) method), as well as by non-contact ones (photothermal radiometry (PTR)). The importance of signal normalization using appropriate reference samples and that of correction by background subtraction is particularly stressed.

(Received June 29, 2000; Accepted November 22, 2000)

Reports on structure investigation of multilayer samples by means of various photothermal methods that rely on the contrast between thermophysical and/or optical properties of the layers have been published in the past.<sup>1-8</sup> Numerous packaging materials are coated with a thin transparent layer (polymer varnish) atop the paper or polymeric substrate. In the dedicated packaging industry there is a need for a method capable of accurately controlling varnish layer thickness within the 0.1-100 μm range. The difficulty resides in the fact that the thermal properties of varnish and substrate are similar, and the optical properties of the layers are not well defined: semi-transparent varnish, scattering and not totally opaque substrate, diffuse reflectance of the whole sample.

In a search towards the best approach in solving the above problem, a comparative study using different techniques (photoacoustics (PA), photothermal radiometry (PTR) and photopyroelectric (PPE)) on identical samples was carried out in different laboratories.

### Theory

The front-detection configuration used in this work is shown schematically in Fig. 1. The measurement principle is based on the assumption that the varnish layer (m) is transparent and the substrate layer (s) is opaque to the incident radiation (VIS-NIR), and that the varnish (m) is opaque in the IR range. The periodic exciting radiation is absorbed at the varnish-substrate (m/s) interface. The surface temperature change  $T_m$  is due to thermal wave propagation from the (m/s) interface through the varnish up to the surface, where it is detected by the photothermal methods mentioned above.

The expression of the temperature modulation  $T_m$  of the sample surface, assuming one-dimensional heat propagation across a two-layer system suspended in air, is the following:

$$T_m = \frac{(1-i) H_0 e^{-\sigma_m L_m}}{4 \sqrt{\pi f} e_c} \cdot \frac{1 + e^{-2\sigma_s L_s}}{1 - e^{-2\sigma_s L_s}} \quad (1)$$

where  $H_0$  is the radiation intensity,  $L_i$  the layer thickness,  $\sigma = (1+i)/\mu$  is the complex thermal diffusion coefficient with  $\mu = (\alpha/\pi f)^{1/2}$  the thermal diffusion length, and  $\alpha$  and  $e$  the thermal diffusivity and effusivity, respectively. For usual packaging materials the last factor in eq.(1) is equal to unity at frequencies above 10 Hz, when the substrate is thermally thick.

The PA, PTR or PPE signals are proportional to  $T_m$ . In practice, it is convenient to normalize the signals of the samples to the one obtained with an opaque reference sample without coating ( $L_m=0$ ). Then, from eq(1) one has:

$$S_n = k \exp[-(1+i)L_m/\mu_m] \quad (2)$$

where the constant  $k$  contains the effusivity ratios and the fractions of radiation absorbed by each sample.

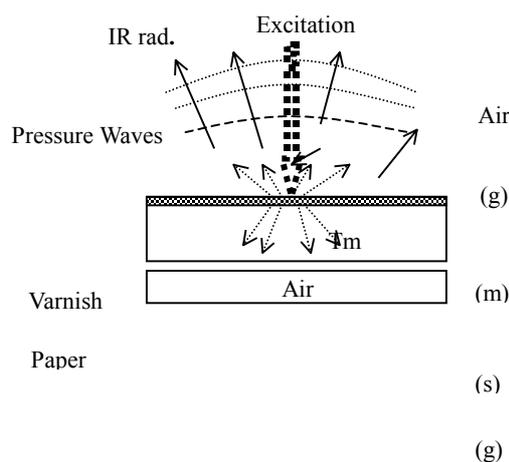


Fig. 1. Schematic representation of photothermal phenomena taking place in a two-layer system. The coating layer (m) is transparent for the excitation and it is opaque in the IR. The (m/s) interface is opaque.

From eq.(2), the normalized amplitude and phase can be written as:

$$\log_e|S_n| = \varphi_n = -L_m(\pi/\alpha_m)^{1/2} f^{1/2} = (\text{slope}) f^{1/2} \quad (3)$$

and  $L_m$  can be determined as:

$$L_m = -(\text{slope}) (\alpha_m/\pi)^{1/2} \quad (4)$$

In order to assure good data quality, the amplitude and phase slopes should be equal. We have used the average slope obtained from amplitude and phase data.

## Experimental

The PTR and PA experimental set ups used either a 30 mW diode laser at 833 nm wavelength (NIR) modulated electronically, or an Ar laser emitting up to 500 mW, modulated by an acousto-optical modulator. The signals were measured with computer-controlled digital lock-in amplifiers. The PTR detector was a HgCdTe infrared detector with the peak response at 10  $\mu\text{m}$ . The PA cell, designed and home-made at the Ruhr Univ. Bochum, had a closed volume of about 0.5  $\text{cm}^3$ . The pressure wave (sound) is communicated through a capillar hole in the wall of the cell to a miniature microphone. The samples were pressed with an O-ring against a glass backing plate, which served also to seal off the cell. Opposite to that, a glass window allowed for the irradiation of the sample.

For the PPE method we used a green HeNe laser for excitation and a LiTaO<sub>3</sub> pyroelectric sensor coated with transparent ITO electrodes, in a non-contact front-detection configuration (FPPE)<sup>9</sup>. The sample was supported by the sensor without a coupling fluid in between, and it was irradiated from the bottom through the sensor.

As a feasibility test, first one has measured a self-made two-layer sample consisting of a 75  $\mu\text{m}$  thick transparent polyethylene adhesive tape stuck on 100  $\mu\text{m}$  thick writing paper printed in black with a laser-printer. Other measured samples were a packaging material composed of a metallized polymer substrate with a 25  $\mu\text{m}$  thick polyethylene coating, an aluminium (7  $\mu\text{m}$  thick) and 50  $\mu\text{m}$  thick paper composite substrate with a 3.2  $\mu\text{m}$  thick heat-seal coating on the aluminium side, a polypropylene substrate printed in green colour with a 1.9  $\mu\text{m}$  thick varnish coating, and a set of paper samples printed in black, having varnish coatings in the range between 1 and 4  $\mu\text{m}$ , as well as a similar black paper without coating for comparison. The reference sample was a nearly-ideal surface absorber (carbon glass) having very large absorption coefficient and optically flat surface.

As alternative methods to determine the coating thickness (called hereafter nominal thickness) we used micrometers and different optical microscopes to image the cross-section of the sample. For some samples the varnish thickness was determined from the specific weight ( $\text{kg}/\text{m}^2$ ) and density ( $1100 \text{ kg}/\text{m}^3$ ) given by the producers. The typical thermal diffusivity of varnish is  $1.22 \times 10^{-7} \text{ m}^2/\text{s}$  and that of polyethylene  $10^{-7} \text{ m}^2/\text{s}$ . For comparison,  $\alpha = 0.65 \times 10^{-7} \text{ m}^2/\text{s}$  for paper. A 10  $\mu\text{m}$  thick varnish coating has the thermally thick/thin limit at 400 Hz.

## Results and Discussion

The surface temperature variation following periodic excitation of an opaque and homogeneous semi-infinite material can be obtained from eq.(1) if  $L_m=0$  and  $L_s/\mu_s \gg 1$ . Then the temperature amplitude varies as  $f^{-1/2}$  and the phase is -45 deg, as illustrated by the PTR signal for carbon glass in Fig. 2. The PA signal has a  $f^{-1}$  dependence and -90 deg phase, due to the additional temperature-to-gas pressure transducing mechanism.

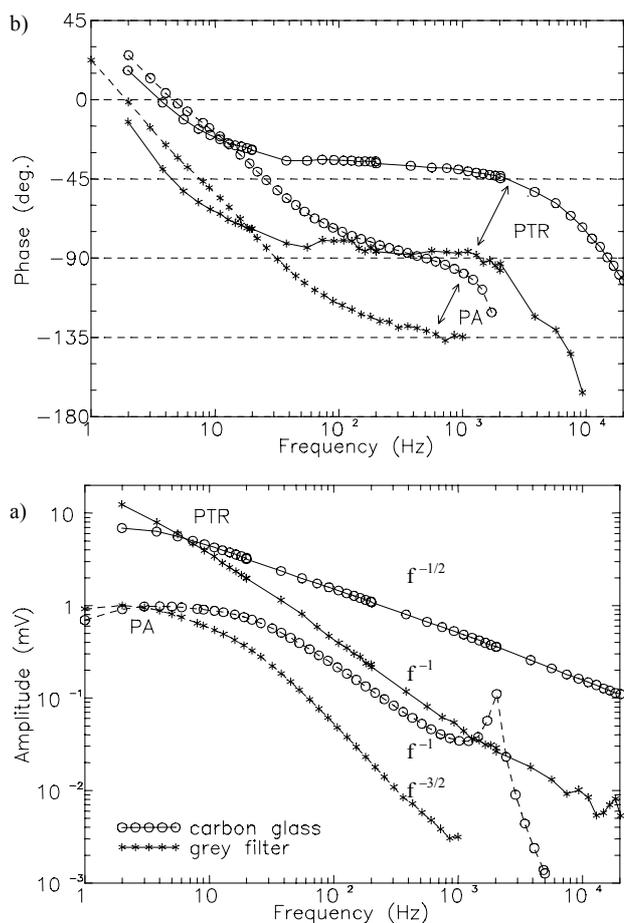


Fig. 2. PTR and PA amplitude (a) and phase (b) for a surface absorber (carbon glass) and for a volume absorber (gray filter).

At low frequency there are deviations from linearity due to microphone and electronics low-frequency limitations, and to two-dimensional heat flow effects. At high frequency, the PA cell has a resonance at 2 kHz, while the bandwidth of the PTR method extends beyond 10 kHz. Fig. 2 also shows the results of a gray semi-transparent glass filter (volume absorber). The theory predicts for  $T_m$  an  $f^{-1}$  amplitude dependence and -90 deg phase, as shown by the PTR signal. The PA signal has a steeper amplitude decrease ( $f^{-3/2}$ ) and larger phase lag (-135 deg).

Fig. 3 shows the experimental results on the test sample and on the black paper, normalised to the carbon glass reference. Most non-linear effects are cancelled out effectively by the normalization procedure, but the black paper still has a weak slope, and the phase is lower than 0 deg. This behaviour cannot be explained by a multi-layer model (e.g. finite thickness of the paper or semi-transparent ink layer), but possibly by a fractal structure of the sample, due to surface roughness.<sup>10, 11</sup>

The signal for the test sample behaves as expected from eq.(2) up to 60 Hz. At higher frequency the background signal follows the one of the bare paper, attenuated by a factor  $m$ . It follows that the results can be improved by normalization to the signal  $S_{\text{ref}}$  obtained with the substrate alone instead of the carbon glass, and by correction for the background signal by vector subtraction:

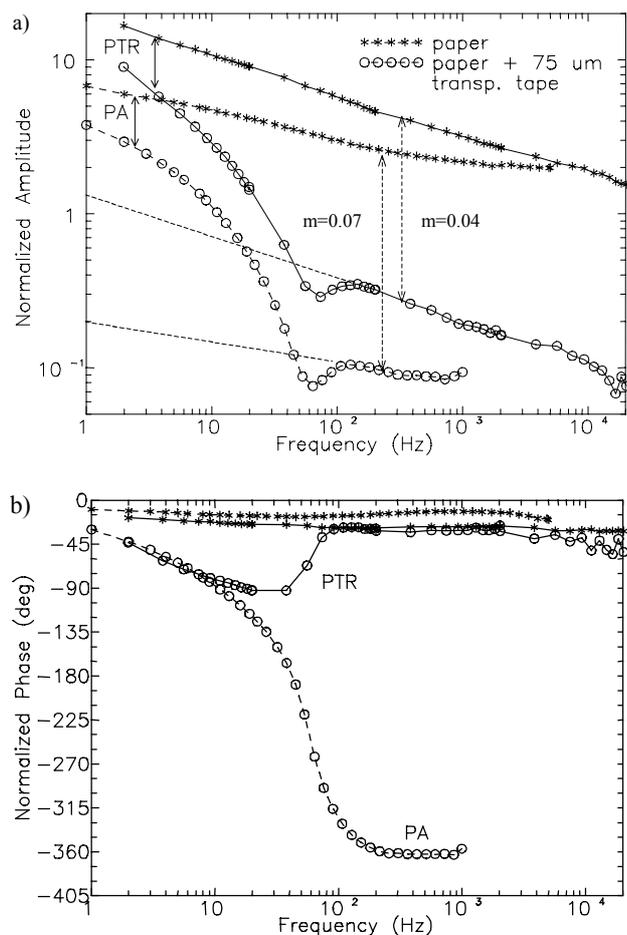


Fig. 3. PTR and PA amplitude (a) and phase (b) for bare and coated black paper (test sample) normalized to a carbon glass reference.

$$S_n = (S_s/S_{ref}) - m. \quad (5)$$

The effect of this procedure on the PA signal of Fig. 3 is shown in Fig. 4. The corrected signals have an improved linearity over a wider frequency range and the difference between amplitude and phase slopes is reduced.

The experimental results obtained in different laboratories on the paper samples with thin varnish layers are shown in Fig. 5. In this case the useful frequency range is shifted to higher frequency and the subtraction of the background was not possible since the factor  $m$  could not be determined. For each sample, the difference between the amplitude and phase slope was less than  $\pm 10\%$ .

The results for samples with coatings in the range between 1.5 and 75  $\mu\text{m}$  are shown in Fig. 6. The dashed line represents the ideal calibration curve (slope = 1). The largest errors are seen for the sample with aluminium substrate (high diffuse reflectance and low absorption) and for the one with the green substrate (not really opaque). In these cases reference samples without varnish were not available and the results were normalized to the carbon glass sample.

The results for paper samples with varnish layers between 1 and 4  $\mu\text{m}$  are given in Fig. 7. The influence of humidity on these samples was reported in Ref. 12. The measured thicknesses are systematically underestimated by an average factor of 0.7 because the assumptions of the model regarding the optical properties of the layers are not entirely fulfilled. Also, the background correction would increase the slopes in Fig. 5, thus yielding larger thicknesses. The three linear fits have slopes between 0.5 and 0.9 with  $\pm 10\%$  error.

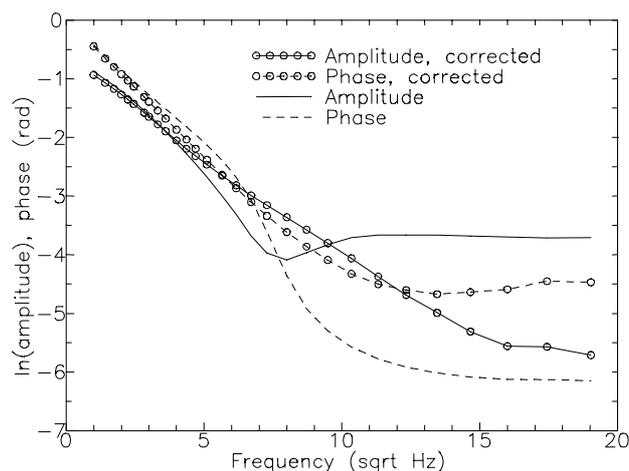


Fig. 4. Coated paper normalized to bare paper using the respective PA signals of Fig. 4, plotted according to eq.(3). The background correction was made with eq.(5).

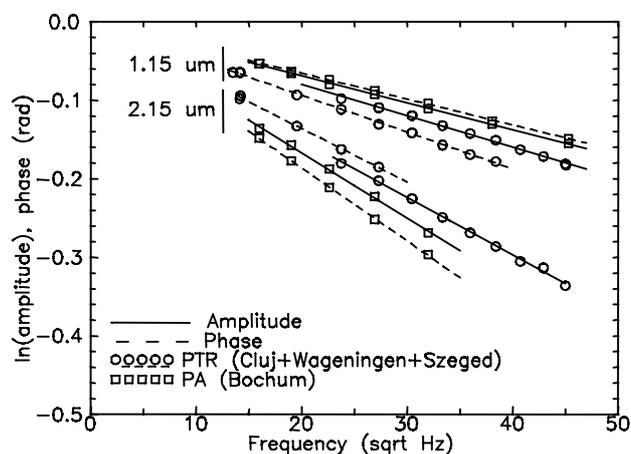


Fig. 5. Experimental results and linear fits of PTR and PA signals obtained in different laboratories for black paper with nominal varnish thicknesses of 1.15  $\mu\text{m}$  and 2.15  $\mu\text{m}$ .

In both Figs. 6 and 7, the thicknesses obtained by PTR are on the average lower than those obtained by PA. The cause might be the partial transparency of the varnish layer to IR radiation, yielding a higher signal in PTR measurements.

The PPE signals for varnished papers are similar to the ones in Fig. 5 but with a lower S/N ratio. The reproducibility of the slope values depends on the pressure applied to the sample to keep it in contact with the sensor. The estimated thicknesses are within  $\pm 50\%$  of the nominal thicknesses.

The results of this work allow to conclude that transparent coating thicknesses of packaging materials can be measured down to 1  $\mu\text{m}$  with fractions of micron resolution. The investigated samples had various substrates, like paper, printed or metallized polymer, aluminium foil. It was shown that the measurements were still consistent under difficult conditions, like for strongly reflecting or scattering substrates. However, for good results, there are some requirements that must be met:

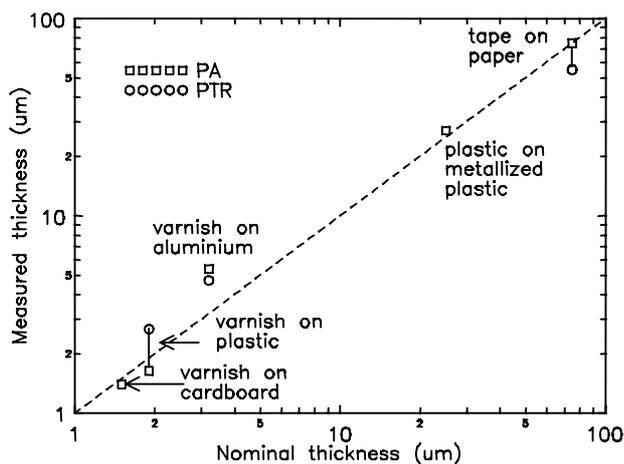


Fig. 6. Measured versus nominal coating thickness for different samples, obtained with the PTR and PA method. The dashed line represents the ideal calibration curve.

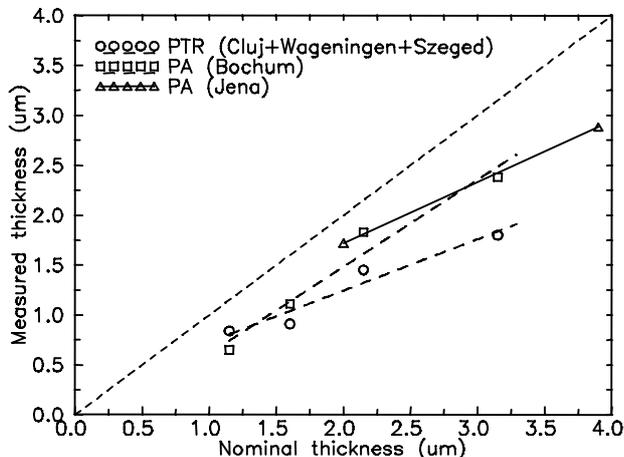


Fig. 7. Same as Fig. 6, for paper samples with thin varnish coating. Results obtained in different laboratories by the PTR and PA method.

- good optical contrast between transparent coating and opaque (preferably black) substrate;
- availability of a reference sample consisting of the substrate alone without coating;
- experimental calibration of each photothermal set up with standard samples having known coating thickness.

The PA method is more sensitive and has a better S/N ratio than the PTR one, for comparable excitation power, while the PTR method has a wider frequency range. The application of the PPE method is limited by the necessity of good thermal contact with the sample.

We are aware of the fact that the achieved accuracy and resolution, as well as the incompatibility of the present laboratory set ups with moving samples in industrial environment, are limiting factors for on-line measurements on production lines. A possible solution might be a photothermal scheme with pulsed excitation and remote radiometric detection.

## Acknowledgement

This work was performed within the frame of the European Thematic Network "Control of Migration by Photothermal Methods", contract no. BRRT-CT98-5041 and IC20-CT98-0002

## References

1. P. Helander, I. Lundstrom and D. McQueen, *J. Appl. Phys.*, **1981**, 52, 1146.
2. H. Coufal and P. Hefferle, *Appl. Phys.*, **1985**, A38, 213.
3. A. Harata and T. Sawada, *J. Appl. Phys.*, **1989**, 65, 959.
4. L. C. Aamodt, J.W. Maclachlan Spicer, and J.C. Murphy, *J. Appl. Phys.*, **1990**, 68, 6087.
5. C. Glorieux, J. Fizev and J. Thoen, *J. Appl. Phys.*, **1993**, 73, 684.
6. E.Y. Jiang, R.A. Palmer and J.L. Chao, *J. Appl. Phys.*, **1995**, 78, 460.
7. R.E. Imhof, A.D. McKendrick and P. Xiao, *Rev. Sci. Instrum.*, **1995**, 66, 5203.
8. M. Munidasa, A. Mandelis and M. Ball, *Rev. Sci. Instrum.*, **1998**, 69, 507.
9. J.S. Antoniow, M. Chirtoc and M. Egee, *J. Phys. D: Appl. Phys.*, **1997**, 30, 1934.
10. B.K. Bein, S. Krueger and J. Pelzl, *Can. J. Phys.* **1986**, 64, 1208.
11. D. Vandembroucq, A.C. Boccara and D. Fournier, *Journal de Physique IV*, **1994**, C7, 331.
12. A. Christ and H.G. Walther, in this volume.