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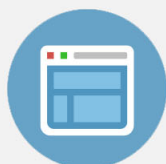
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Photoacoustic procedure for measuring thermal parameters of transparent solids

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An application of photoacoustic technique is developed for determining the thermal diffusivity coefficient and the thermal conductivity of transparent materials. The backing material which supports the sample is made optically opaque, i.e., it entirely absorbs the incident light, and the converted heat diffuses through the sample heating the gas in contact with its opposite surface. The method is illustrated by fitting voltage amplitude and phase signals versus the chopping frequency in the photoacoustic cell, according to a theoretical model of heat diffusion. Thermal parameters obtained for three polymers compare very well with results from the literature. © 1995 American Institute of Physics.

Photothermal phenomena in solid materials are generated by a combination of thermal expansion, thermal diffusion, and thermoelastic bending effects.¹⁻⁴ One of these mechanisms may predominate depending on the particular material and/or on the experimental conditions. A possible way of distinguishing among these effects is the use of photoacoustic techniques (PA), in particular by investigating the PA dependence on the modulated chopping frequency of the incident light beam f . These techniques are versatile, nondestructive, and can be employed under different experimental conditions for determining thermal parameters of solid materials. Several photoacoustic cells with slight modifications,⁵⁻⁸ including the derivative photopyroelectric^{8,9} and photothermal deflection¹⁰ methods, have been used in some special cases with great success.¹¹⁻¹³ The apparatus for all techniques is basically the same, the modifications being mainly concentrated on the type of detector and on its location relative to the sample inside the cell. In all cases, the photothermal signal depends on the material thermal properties as well as on the geometry of the sample. In this letter, we propose an efficient photoacoustic procedure for the thermal characterization of transparent samples, which was applied to polymeric films of poly(vinylidene fluoride) (α -PVDF), poly(methyl methacrylate) (PMMA), and poly(vinyl chloride) (PVC).

Figure 1 shows a schematic diagram of the closed photoacoustic cell on which a pulsed light beam is impinged. The cell comprises a transparent window (w), a gas medium (g) (air in this case), the sample (s), a backing material (b), and a microphone (M) as the acoustic detector. All polymeric samples were obtained from commercial products. PVDF samples (manufactured by Bemberg Folien GmbH) with density equal to 1.76 g/cm^3 were obtained from films slightly stretched. PMMA samples were cast from a toluene solution of PMMA powder (ICI-Acrylics) and a density of $\sim 1.21 \text{ g/cm}^3$. PVC samples with density of 1.39 g/cm^3 were obtained by pressing a PVC powder (Norvic) at 250°C , followed by quenching to room temperature. In all cases, manu-

facturers mention that the material (film or powder) were made by molecules of high molecular weight.

A He-Ne laser beam is used as the light source which is modulated by a chopper with an automatic frequency control. The signal is amplified by a low-noise preamplifier and then measured by a lock-in amplifier. The normalized signal V_N is the ratio between the voltage of the PA cell and the reference cell voltage (without the sample). The thermal parameters are obtained by fitting the experimental data according to a model of heat diffusion in the PA cell. Several assumptions are implicit in the model: (i) The sample is transparent to the incident light; (ii) the diffusion is unidimensional since the lateral dimensions of the cell are much larger than the thickness of the whole setup; (iii) the heat is entirely generated in the backing material and diffuses back through the sample; and (iv) the thermal diffusion is dominant in the heat transport. The equations which govern the heat diffusion in the PA cell are:

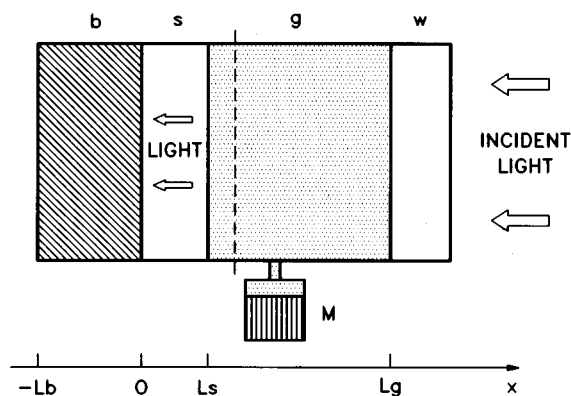


FIG. 1. One-dimensional geometry of the photoacoustic setup.

$$\begin{aligned} \frac{\partial^2 T_g}{\partial x^2} - \sigma_g^2 T_g &= 0, \quad L_s \leq x \leq (L_s + L_g) \\ \frac{\partial^2 T_s}{\partial x^2} - \sigma_s^2 T_s &= 0, \quad 0 \leq x \leq L_s \\ \frac{\partial^2 T_b}{\partial x^2} - \sigma_b^2 T_b &= -\left(\frac{\eta_b \beta_b I_0}{2k_b}\right) \exp(\beta_b x), \quad x \leq 0, \end{aligned} \quad (1)$$

where T_i is the temperature, σ_i the complex thermal diffu-

sion coefficient, L_i the thickness, k_i the thermal conductivity, β_i the optical absorption coefficient, and η_i the efficiency conversion factor from light-to-heat (for $i = g, s$, or b). I_0 is the intensity of the incident laser beam. The objective is to derive the expression for the pressure variation detected by the microphone. Following the procedure established by Rosencwaig¹⁴ with the condition that the backing material is thermally thick, we obtain

$$T_g = \frac{1}{2\sqrt{2}\pi} \left(\frac{\eta_b r_b I_0}{k_b \sigma_b (r_b + 1)} \right) \frac{b_{bs} \exp i(\omega t - \pi/4)}{(b_{gs} + 1)(b_{bs} + 1) \exp(\sigma_s L_s) - (b_{gs} - 1)(b_{bs} - 1) \exp(-\sigma_s L_s)}, \quad (2)$$

where ω is the chopping angular frequency, $r_i = \beta_i / \sigma_i$ is the optical-thermal parameter, and $b_{ij} = k_i \sigma_j / k_j \sigma_i$ ($j \neq i$) is the thermal coupling parameter between the materials i and j . When the gas is adiabatic and considering that in the depletion region, which is defined by $2\pi\mu_g$ (μ_g is the thermal diffusion length of the gas), the displacement is given by $\Delta x(t) = 2\pi\mu_g T_g(t) / T_0$ (T_0 is the room temperature), the pressure variation is

$$\Delta P(t) = \frac{2\pi\mu_g \gamma P_0}{L_g} \frac{T_g(t)}{T_0}. \quad (3)$$

P_0 is the room pressure and γ is the adiabatic coefficient. In the following we discuss special cases, for which Eq. (3) is drastically simplified and becomes more adequate for particular applications.

Case 1: The backing material is optically thick ($r_b \gg 1$) and the thermal couplings $b_{gs} \ll 1$ and $b_{bs} \ll 1$, which means that the sample is more thermally conductive than the air and the backing material. The complex amplitude of the photoacoustic signal is, therefore:

$$Q \approx \frac{A\mu_g}{k_b \sigma_b} \left(\frac{2b_{bs}}{\sinh(\sigma_s L_s)} \right), \quad (4)$$

where $A = (\gamma\eta_b P_0 I_0) / (\sqrt{2}L_g T_0)$. In addition, if the sample is considered thermally thick, the amplitude Q and the phase signal ϕ are given, respectively, by

$$Q \approx A\mu_g \frac{b_{bs}}{k_b \sigma_b} \exp(-\sigma_s L_s)$$

and

$$\phi = -\sqrt{\frac{L_s^2 \omega}{2\alpha_s}} - \frac{\pi}{2}. \quad (5)$$

As one can observe ϕ is a linear function of $\omega^{1/2}$, while the amplitude obeys a ω^{-1} relation because the thermal diffusivity coefficient σ is proportional to $\omega^{1/2}$.

On the other hand, if the sample is thermally thin ($\sigma_s L_s < 1$), the amplitude is a constant factor equal to $\pi/2$, and the amplitude is

$$Q \approx A\mu_g \frac{2b_{bs}}{k_b \sigma_b \sigma_s L_s}. \quad (6)$$

The amplitude Q varies with the angular frequency according to a $\omega^{-3/2}$ function.

Case 2: Similar conditions of case 1, but now the backing material is a better thermal conductor than the sample, i.e., $b_{bs} > 1$. In this case, with the additional condition of a thermally thick sample, i.e., $(b_{bs} + 1) \exp(\sigma_s L_s) > (b_{bs} - 1) \exp(-\sigma_s L_s)$, the photoacoustic signal is given by

$$Q \approx A\mu_g \frac{b_{bs}}{k_b \sigma_b (b_{bs} + 1)} \exp(-\sigma_s L_s). \quad (7)$$

Analogously to Eq. (5), Q also varies with ω^{-1} . The reference signal amplitude $Q_R \approx A\mu_g / 2k_b \sigma_b$ ($\phi = -\pi/2$), which is equivalent to the very thin sample situation, is used to obtain the normalized signal $V_N = Q / Q_R$. Therefore, Eq. (7) can be written as

$$V_N = \frac{2b_{bs}}{b_{bs} + 1} \exp(-\varphi_s \sqrt{\omega}), \quad (8)$$

where φ_s is a coefficient which contains the thickness and the thermal diffusivity of the sample ($\varphi_s = \sqrt{L_s^2 / 2\alpha_s}$). It is important to remark that b_{bs} is expressed in terms of both the thermal diffusivity and the thermal conductivity of the sample and the backing material ($b_{bs} = k_b \alpha_s^2 / k_s \alpha_b^2$). The phase signal varies with the frequency in a law similar to that presented in Eq. (5).

Figure 2 shows measurements of the normalized amplitude signal carried out with three transparent films to polymeric materials: α -PVDF, PMMA, and PVC. All samples were circular with 8 mm in diameter; their face in contact with the backing material is painted with black ink to ensure a perfect optically thick condition of the backing material. The thickness of the samples were 50, 30, and 9 μm , for PVDF, PMMA, and PVC, respectively. A He-Ne laser beam is modulated by a chopper of controlled frequency. The signal is improved by a low-noise preamplifier and then measured by a lock-in amplifier. The amplitudes decay as the

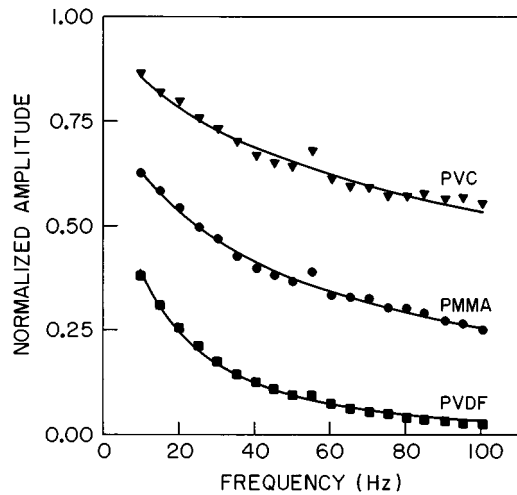


FIG. 2. Experimental (dots) and calculated (continuous line) values of the photoacoustic voltage frequency response of transparent polymeric materials.

chopping frequency increases. Since the samples are thermally thick and bad thermal conductors, the fitting was performed with Eq. (8). The experimental results of phase signals ϕ , showed a linear dependence with the square root of the chopping frequency (ϕ vs $f^{1/2}$, $f = \omega/2\pi$) for the three transparent polymers, and they were fitted by Eq. (5) as shown in Fig. 3. The thermal diffusivity coefficient α_s , and the thermal conductivity k_s , were used as parameters in both amplitude voltage and phase curves. Their values are presented in Table I which compare well with values published in the literature.

The thermal conductivity of the polymeric materials depends strongly on their density (which is equivalent to its degree of crystallinity). Polyethylene, for example, has its

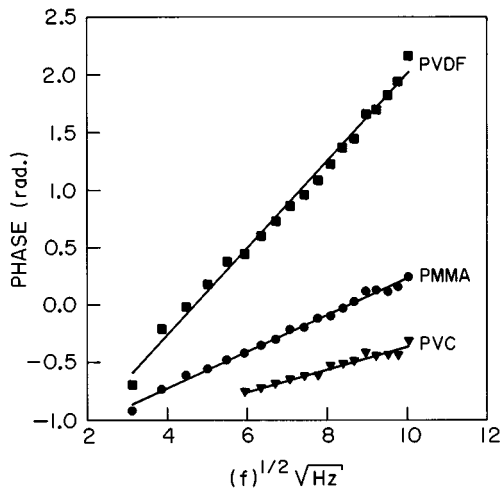


FIG. 3. Experimental (dots) and calculated (continuous line) values of the photoacoustic phase frequency response of transparent polymeric materials.

TABLE I. Thermal diffusivity coefficients and thermal conductivities obtained from the fitting of Figs. 2 and 3. For comparison values of the literature are presented.

Materials	α (10^{-8} m ² /s)	α_{lit} (10^{-8} m ² /s)	k (W/mK)	k_{lit} (W/mK)
PVDF	5.5(ϕ)	5.4 ^{a,b}	0.10	0.13 ^b
PMMA	11.1(ϕ)	11.4 ^{a,c}	0.25	0.193 ^c
PVC	5.55(A)	5.93 ^d	0.12	0.15 ^c

^aThe relation $\alpha = k/\rho c$ was used for determining the thermal diffusivity coefficient. c is the heat capacity.

^bKynar Piezo Film Technical Manual, Pennwalt Corp. 900 First Ave., King of Prussia, PA, p. 17 (1983) (density $\rho_{PVDF} = 1.8$ g/cm³).

^cPolymer Handbook, 2nd. ed., edited by J. Brandup and E. H. Immergut (Wiley, New York, 1980). ($\rho_{PMMA} = 1.19$ g/cm³ and $\rho_{PVC} = 1.44$ g/cm³).

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room-temperature thermal conductivity increased by a factor two¹⁵ when the density varies from 0.92 to 0.98 g/cm³. This density dependence may explain differences in our experimental values compared to those in the literature, as shown in Table I. It is also important to remark that the thermal parameters (k_s and α_s) are sensitive to thermomechanical sample treatment (extrusion and blowing processes) which may cause different orientations in the polymeric structures. On the other hand, molecular weight and the syndiotactic nature of polymeric solids plays a minor influence on thermal conductivity.

In conclusion, the photothermal technique has been shown to be a versatile technique which may be adapted for the materials according to their characteristics, or even the properties under investigation. This makes it possible to simplify operational procedures, without losing accuracy. When applied to transparent materials, as was the case of the transparent polymeric samples (PVDF, PMMA, and PVC), photoacoustic methods allow important thermal parameters to be obtained in a very fast fashion.

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