Determination of thermal and optical parameters of melanins by photopyroelectric spectroscopy

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Photopyroelectric spectroscopy (PPE) was used to study the thermal and optical properties of electropolymerized melanins. The photopyroelectric intensity signal and its phase were independently measured as a function of wavelength, as well as a function of chopping frequency for a given wavelength in the saturation part of the PPE spectrum. Equations for both the intensity and the phase of the PPE signal were used to fit the experimental results. From the fittings we obtained for the first time, with great accuracy, the thermal diffusivity coefficient, the thermal conductivity and the specific heat of the samples, as well as a value for the condensed phase optical gap, which we found to be 1.70 eV. © 2005 American Institute of Physics. [DOI: ]

The melanins are a class of bio-macromolecule found throughout nature.1 In humans, they act as pigments and photoprotectants in our hair, skin and eyes. They are also found in the brain stem and inner ear, where their roles are less well defined. Eumelanins (also known as dopa-melanins), the predominant form of the macromolecule in humans, are broad band ultra-violet and visible light absorbers. Additionally, they are the only known solid state bio-macromolecule semiconductor.2 This combination of properties has led to the novel proposition that they may be useful from a technological perspective as functional “electronic soft-solids”.1 Despite significant scientific effort over the past 30 years, large knowledge gaps concerning the basic physics and chemistry of melanins still exist. These materials are particularly intractable from the analytical perspective, since they are chemically and photochemically very stable, and virtually insoluble in most common solvents. Hence, we do not fully understand key properties such as electronic structure vs. chemical composition, or why (and how) melanins conduct electricity in the condensed solid state. Significant knowledge gaps also exist regarding melanin biofunctionality. It is well accepted that these molecules serve as our primary photoprotectants. However, the mechanisms by which melanin aggregates dissipate potentially harmful solar radiation are not well understood. It has been proposed that efficient coupling between photo-excited electrons and phonon modes allows non-radiative dissipation of absorbed photon energy – i.e. melanins can effectively turn biologically harmful photons into harmless heat.

Photothermal spectroscopic (PTS) techniques have been extensively and successfully applied to solid state materials for obtaining their thermal and optical parameters.4−6 In these techniques a pulsed light beam is absorbed in a solid sample and the converted heat (non-radiative conversion) diffuses into the bulk structure; the sample expansion, or the temperature gradient, is then detected by an appropriate sensor system. The detected signal depends on the optical and thermal properties of the sample: the optical absorption coefficient β(λ) (λ being the light wavelength), the non-radiative conversion efficiency η(λ), the thermal conductivity k, and the thermal diffusivity coefficient α. The signal also depends on experimental control parameters such as the chopping frequency f of the incident light beam. Among the PTS techniques, photoacoustic spectroscopy (PAS),7 which is the most traditional one, and the more recent photopyroelectric spectroscopy (PPES) have been used for studying thermal and optical properties of polymeric films.8−11 Among the various physical parameters which can be measured, the thermal diffusivity is particularly important because this measurement allows one to obtain the thermal conductivity and specific heat. Furthermore, the importance of this measurement resides in the fact that, as with the optical absorption coefficient, the thermal diffusivity is unique for each material. When the thermal conductivity is known, information can be obtained regarding the heat transfer process by phonons and by carriers (electrons or holes). In this current study, we used samples of electropolymerized (EP) melanins on indium tin oxide (ITO) glass and compressed powder as self supporting pellets. Equations for both the intensity and the phase of the PPE signal, taking into account the thermal and the optical characteristics of the pyroelectric detector, have been used to fit the experimental results.

The detected signal V(ω,t), ω=2πf, is proportional to the pyroelectric coefficient p of the detector and to the temperature distribution along the detector thickness:8−13

\[ V(\omega,t) = \frac{p}{K_{\infty}} \int_{-L/2}^{L/2} T_{\omega}(x,t) \, dx \, e^{i\omega t} \]  

where \( L_p \) is the sample thickness, \( T_{\omega}(x,t) \) the temperature of the sample, k the dielectric constant of the material, i = (−1)\( \lambda \), and \( \varepsilon_0 \) the vacuum dielectric permittivity. The heat propagation across the whole chamber is governed by heat diffusion equations of each medium coupled via boundary conditions at the interfaces (\( T_\omega = T_b \) and \( k_\omega \partial T/\partial x = k_b \partial T_b/\partial x \), a and b representing consecutive media), as established by Mandelis and Zver.12 The signal V(ω,t) obtained by integrating the diffusion equations is normalized by the ratio V(ω,t)/V_b, where V_b is the signal measured directly over the detector painted with a very thin layer of a black ink. In this latter case, the detector is considered thermally thick and optically opaque, and the normalized voltage signal as given in Refs. 8–13.

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Assuming the case where the sample is in an optically opaque condition, that is, in the saturated region of the spectra, then the normalized voltage and phase signal can be expressed as:

\[ V_n(a) = 2q \left( b_s + b_p \right) \]
\[ \pm \left( (b_p + 1)(b_s + 1)e^{\pi i a} - (b_p - 1)(b_s - 1)e^{-\pi i a} \right) \]

\[ F_n(a) = -\arctan \left( \tan(a) L_n \right) \]

where:

\[ y = \frac{(b_s b_p + 1) \cosh(a L_n) + (b_s + b_p) \sinh(a L_n)}{(b_s + b_p) \cosh(a L_n) + (b_s b_p + 1) \sinh(a L_n)} \]

and where \( \alpha_q = (1 + i)\alpha_a \) with \( \alpha_a = (\pi f / \omega_a) \)

The PPE cell was set up with a silica window above the sample for the melanin pellets, and for the EP films the sample for the melanin pellets, and for the EP films the EP melanin film. The PPE spectral data were recorded in the stationary state. The values of \( \gamma \) in Eq. (3) were then used for the simple relation \( F_n \propto \alpha_q \). As such, the thermal diffusivity \( \alpha_q \) is directly derived from the slope of the fitting curve \( F_n \) vs. \( f \) (the continuous line of Fig. 2), using the relation \( \alpha_q = (\pi f / \omega_a)^{-1} \), and its value is shown in Table I.

The \( \alpha_s \) values of Table I were then used for the \( V_n(f) \) fitting utilizing Eq. (2), and the thermal conductivity \( k_s \) became the single adjusted parameter of the results shown in Fig. (3). The specific heat of the sample \( c_s \) is directly obtained from the slope of the fitting curve \( F_n \) vs. \( f \) (the continuous line of Fig. 2), using the relation \( \alpha_q = (\pi f / \omega_a)^{-1} \), and its value is shown in Table I.

The \( \alpha_q \) values of Table I were then used for the \( V_n(f) \) fitting utilizing Eq. (2), and the thermal conductivity \( k_s \) became the single adjusted parameter of the results shown in Fig. (3).
consistent with the fact that the sample is optically opaque below 730 nm. In this case, the phase lag is greater in the region with higher opacity, and the normalized phase spectrum follows an absorption behavior as depicted in Fig. 5. Hence, from these spectra, we can conclude that the optical gap of the EP melanin starts at around 730 nm, i.e., 1.70 eV.

![Graph](image1)

**FIG. 2.** Experimental points (dots) and line of best fit for the PPE normalized phase.

![Graph](image2)

**FIG. 3.** Experimental points (dots) and line of best fit for the PPE normalized voltage.

![Graph](image3)

**FIG. 4.** PPE normalized voltage $V_n$ spectrum of the 65 µm EP melanin film.

In conclusion, in this paper we have presented the application of a particular photothermal technique, photopyroelectric spectroscopy, in thermal and optical studies of melamins. Despite the complexity of the PPE equations, establishing the optically opaque condition makes the theoretical approach a realistic tool to fit the experimental curves. The values given in Table I for a melanin pellet show a thermal diffusivity and a thermal conductivity near to that of insulating polymers, but a significantly lower specific heat. More importantly, our data indicates that these melanin samples possess a solid state optical gap of 1.70 eV. This value corresponds to the minimum energy required to cause a transition between the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO respectively) of the system. As such, it corresponds to the HOMO-LUMO gap and is consistent with our first principles density functional theory calculations of the gap of indolequinone and hydroxyindole oligomers.15 We believe our measurements to be the first direct observation of the optical gap of melanin, and its determination will undoubtedly assist in ongoing effort to understand the condensed phase physics and chemistry of these important bio-materials.

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