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 melanins. The photopyroelectric intensity signal and its phase were independently measured as a function of wavelength and 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 these fits 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: 10.1063/1.2009833]

The melanins are a class of biomacromolecules found throughout nature. In humans, they act as pigments and photoprotectants in our hair, skin, and eyes. Eumelanins, the predominant form of the macromolecule in humans, are broadband ultraviolet and visible light absorbers. Additionally, they are thought to be solid state biomacromolecular semiconductors. This combination of properties has led to their use as protective agents against UV and visible light, and as photoreactive agents. Despite significant scientific effort over the past 30 years, melanin-based polymers have not yet been used for studying thermal and optical properties of polymeric films. Of the various physical parameters which can be measured, the thermal diffusivity is particularly important because it allows one to obtain the thermal conductivity and specific heat. 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 the intensity and phase of the PPE signal have been used to fit the results.

The detected signal $V(\omega, t)$, $\omega=2\pi f$, is proportional to the pyroelectric coefficient $p$ of the detector and to the temperature distribution along the detector thickness,

$$V(\omega, t) = \frac{p}{K_{\delta f}} \int_{T_p} T_p(\omega, x) dx e^{i\omega t},$$

where $L_p$ is the detector thickness, $T_p(\omega, x)$ is the temperature field in the bulk of the detector, $K$ is the relative dielectric constant of the detector, $i=(-1)^{1/2}$; and $\varepsilon_0$ is 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 ($T_p = T_0$ and $k_p dT_p/dx = k_0 dT_0/dx$, $a$ and $b$ representing consecutive media), as established by Mandelis and Zver. The signal $V(\omega, t)$ obtained by integrating the diffusion equations is normalized by the ratio $V(\omega, t)/V_R$, where $V_R$ 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, i.e., $\mu_p < L_p$ and $\beta_p^{-1} < L_p$, where $\mu_p = (\alpha_\rho/\pi \mu_\rho)^1/2$ is the thermal diffusion length of the detector, and $\beta_p^{-1}$ is its optical absorption length. Under such circumstances, the expression for the normalized voltage signal is significantly simplified. Assuming the case where the sample is in an optically opaque condition ($\beta_p^{-1} < L_p$), that is, in the saturated region of the spectra, then the normalized voltage and phase signal can be expressed as.
Thin films of dihydroxyphenylalanine eumelanin were synthesized by oxidative electropolymerization of DL-DOPA (Sigma-Aldrich). Initial solutions were 30 mM of DL-DOPA in sodium tetraborate buffer (Sigma-Aldrich, 0.1 M, pH 9). Electrical current was passed through the solutions by dropping up to 20 V across a copper cathode and ITO anode using a dc power supply. To accelerate the formation of melanin, the solution was initially oxidised by mechanical stirring for 10–15 min at a voltage that generated 10–20 mA/cm² of current. The solution was then left in atmospheric conditions at a current density of 0.5 mA/cm² for 1–8 days, depending on the desired thickness of the film. During this time, the solution turned black and a soft black melanin film formed on the anode. Once the desired thickness was achieved, films were dried slowly in a sealed container with various saturated salt solutions to control the relative humidity. The humidity was stepped down from 94% to about 50% over a period of 3–5 days. Slow drying minimised cracking of the films. In the course of drying, the films decreased in thickness from about 100–500 µm to 1–2 µm for the thinnest films. We obtained samples with various thicknesses, ranging from ~1 to 65 µm. Synthetic powders of eumelanin were extracted from the black, electropolymerized DL-DOPA solutions by acidification to pH 2.0 with 6 M hydrochloric acid. The precipitated melanin was separated from the solution by centrifuging at 3500 rpm for 10 min and then dried in air. Powders were pressed at 400 MPa into pellets 192–500 µm thick, with the thinnest pellets most suitable for PPE measurements. Pressed pellets and thin melanin films were fabricated in order to provide flexibility with respect to sample thickness, i.e., to ensure that we could access the all important optically opaque regime. Both sets of samples were polymerized under similar conditions, and
showed identical optical absorption behavior, electrical conductivity and microstructure. As such, we believe them to be equivalent.

Figures 2 and 3 show, respectively, the normalized phase $F_n(f)$ and voltage amplitude $V_n(f)$ as a function of the chopping frequency, for the melanin pellet. At the wavelength of the green power source ($\lambda=543.5$ nm), the sample is highly absorbing as shown in Fig. 4. The data were recorded in the saturated region of the PPE spectra, for the case where the detector is thermally thick, that is, above 10.7 Hz. The experimental points for the normalized phase obey a linear dependence on the square root of the frequency for frequencies $<120$ Hz (see Fig. 2). This means that the fractional term $\gamma$ [Eq. (4)] in Eq. (3), is approximately unity in this frequency range. In fact, $\gamma$ differs from unity by less than 1%, when we consider appropriate values for thermal conductivity and diffusivity coefficients. This permits us to approximate Eq. (3) to the simple relation $F_n \approx \alpha_s L_s$. As such, the thermal diffusivity $\alpha_s$ is directly obtained from the slope of the fitting curve $F_n$ vs $f^{1/2}$ (the continuous line of Fig. 2), using the relation $\alpha_s = (\pi f L_s)^{1/2}$, 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 derived from the relation $k_s = \rho c_s \alpha_s$, where $\rho$ is the mass density, valid for a stationary state. The values of $k_s$ and $c_s$ found via this analysis are also shown in Table I.

Figure 4 shows PPE spectra at 20 Hz chopping frequency, normalized voltage and phase (inset) of the 65 $\mu$m EP melanin film. The PPE $V_n$ signal follows approximately the optical transmission spectrum of the material, i.e., is transmission-like, but saturates for wavelengths below 730 nm. The $F_n$ spectrum in the inset of Fig. 4 also shows a behavior 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. Hence, from these spectra, we can conclude that the optical gap of the EP melanin starts is approximately 730 nm, i.e., 1.70 eV.

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 hydroxy-indole oligomers. 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 biomaterials.

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| $L_s$ ($\mu$m) | 192±5   |
| $\rho_s$ (g/cm$^3$) | 1.43±0.01 |
| $\alpha_s$ ($m^2/s$) | $(2.96\pm0.05) \times 10^{-7}$ |
| $k_s$ (W/m K) | $(0.106\pm0.002)$ |
| $c_s$ (J/kg K) | $(250\pm7)$ |