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Accurate determination of ultrathin PET film structural disorder and bandgap energy by absorption optical spectroscopy

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RESEARCH AIM

The study of the band structure of solid polymers provides important information on the physical properties of these materials (e.g., structural disorder, bandgap energy, relevance of absorption/fluorescence phenomena, etc.). This information can be obtained by analyzing the dependence of the optical absorption coefficient on photon energy (i.e., **α(E)**). According to the **Lambert law** for homogeneous optical media, the absorption coefficient of a polymeric film at a specific wavelength, α(λ), is related to the absorbance at that wavelength, A(λ), and to material thickness, d. Lambert law is usually expressed as: α(λ)=(ln10)·A(λ)/d. Both parameters in such relationship can be obtained from the absorption optical spectrum (UV-Vis-NIR spectroscopy data) of the polymeric film. Indeed, UV-Vis-NIR spectrum includes interferometric information (spectral oscillations due to the Fabry-Perot effect), that is useful to accurately measure film thickness (in the case the polymer refractive index is known) and interband transition information, that is stated in absorbance form.

Here, it has been shown as the exact spectral positioning of fundamental absorption edge (HOMO-LUMO transition) is strictly related to polymer structure (chemical composition and constitution) and therefore it can be used to identify the polymer type. On the other hand, cut-on (transparent-opaque transition) sharpness depends on structural disorder in the polymer. These two physical quantities are relevant for polymer applications and can be determined by approaches like Urbach and Tauc methods, based on the optical absorption coefficient function, α(E).

OPTICAL ABSORPTION COEFFICIENT *vs.* PHOTON ENERGY

The ultrathin PET film absorbance data in the UV-Vis-NIR spectral regions have been collected by using a dual-beam UV-Vis spectrophotometer (UV-3600PC, VWR). Optical spectra (see Figure 1a,b) show clear evidences of spectral oscillations (interference fringes) and interband transitions.

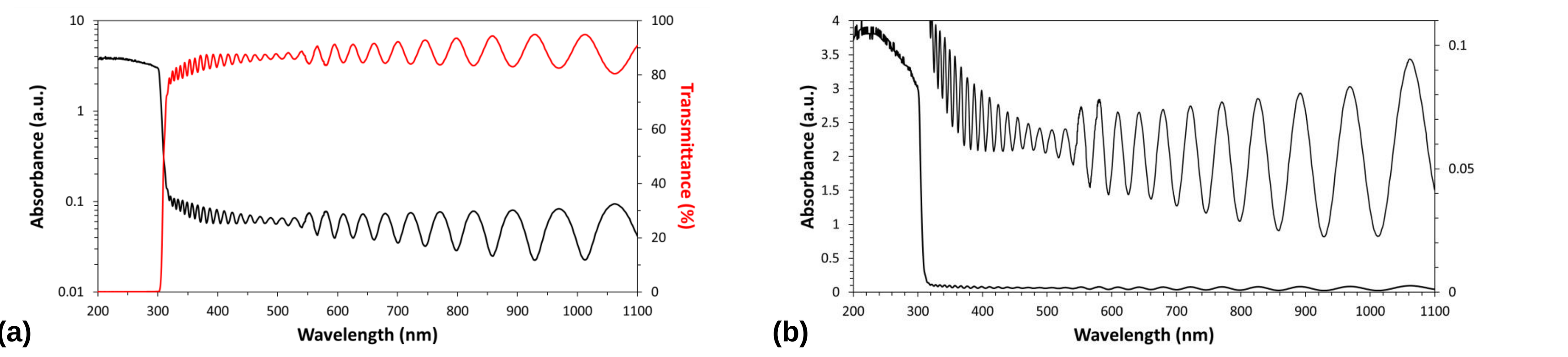


Fig. 1 – Optical absorption data of 'as received' ultrathin PET films, expressed in transmittance (a) and absorbance (b) mode.

The analysis of spectral oscillations has allowed accurate PET film thickness determination (3.665 μm) and this value has been combined with absorbance data to obtain the optical absorption coefficient behavior with photon energy (i.e., α(E)). In particular, interferometric fringes appear in the optical spectra because of Fabry-Perot effect. When the optical path of waves traveling in the film (because of internal reflections) compares with the radiation wavelength (it takes place with few microns thick films), well-resolved spectral oscillations are visible. In addition, polymeric films with high refractive index and perfectly flat surfaces like PET films produce intense spectral oscillations. On the basis of the Fabry-Perot theory, film thickness can be accurately measured by using the wavelength values of constructive/destructive interference. In particular, according to this theory, the optical path for a constructive interference satisfies the condition: **2n·d=m·λ**, where n is the refractive index of the polymeric film (n_{PET}=1.575), d the film thickness, λ the wavelength of fringes maxima and m an integer number (e.g., ±1, ±2, etc.), named interference order. Based on this condition, the following relationship for calculating film thickness from the average interference wavenumber can be derived: **d=Δm/[2n(1/λ₁-1/λ₂)]**, where Δm is the number of oscillations contained in the spectrum between the λ_1 and λ_2 wavelengths (see below the detailed mathematical derivation of this relationship). Alternatively, thickness can be obtained from a plot of 1/λ *vs.* interference fringe numbers (slope of the straight line obtained by linear regression analysis, as shown in Figure 3).

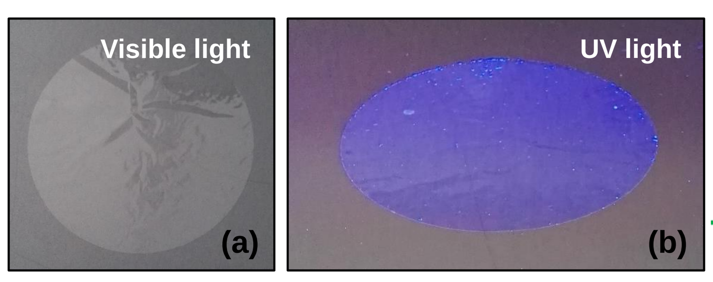
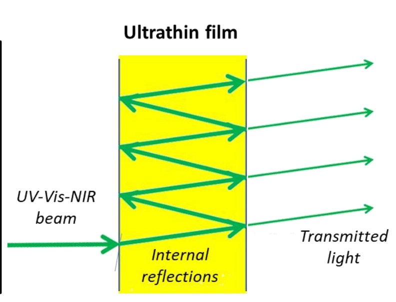


Fig. 2 - Investigated ultrathin PET film under visible (a) and ultraviolet light (Hg-vapor lamp) (b).



$$2nd = m\lambda$$ *Condition for constructive interference*

$$\frac{1}{\lambda} = \left(\frac{1}{2nd}\right)\cdot m$$ *Straight line equation*

$$\frac{1}{2nd} = \frac{\Delta\frac{1}{\lambda}}{\Delta m} = \frac{\frac{1}{\lambda_1}-\frac{1}{\lambda_2}}{\Delta m}$$ *Slope calculation*

$$d = \frac{\Delta m}{2n\left(\frac{1}{\lambda_1}-\frac{1}{\lambda_2}\right)}$$ *Formula for calculating film thickness (n is assumed constant in the investigated spectral range)*

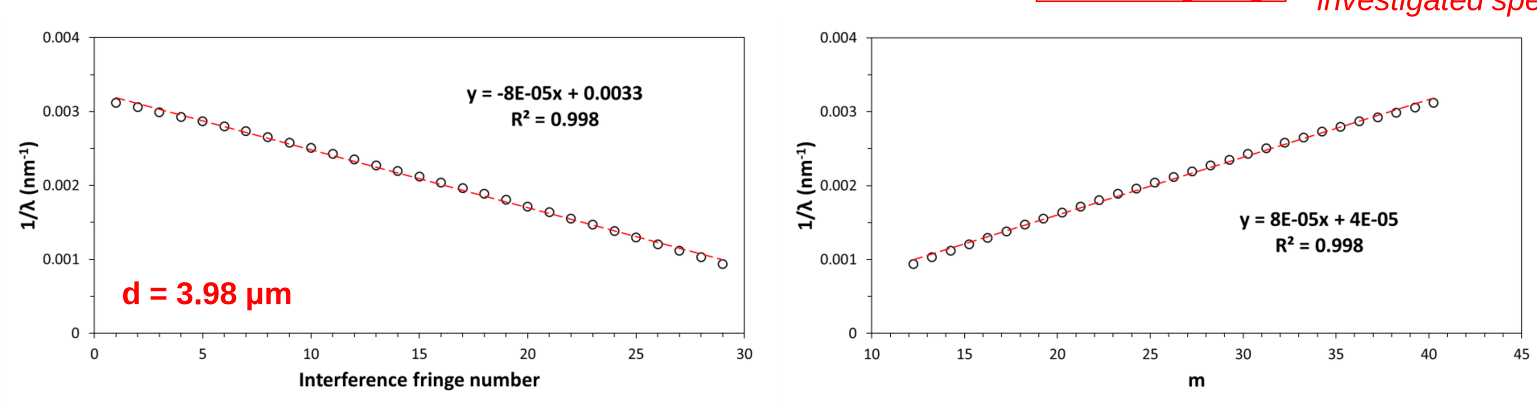


Fig. 3 – Ultrathin PET film thickness estimation by Fabry-Perot effect (both graph types can be equivalently used).

The Fabry-Perot effect can be used to accurately quantify thickness changes undergone by ultrathin PET films under applied tensile stresses (e.g., uniaxial/biaxial manual stretching). Interferogram spectral positioning and fringe spacing visibly modify as a result of the applied stress (see Figure 4).

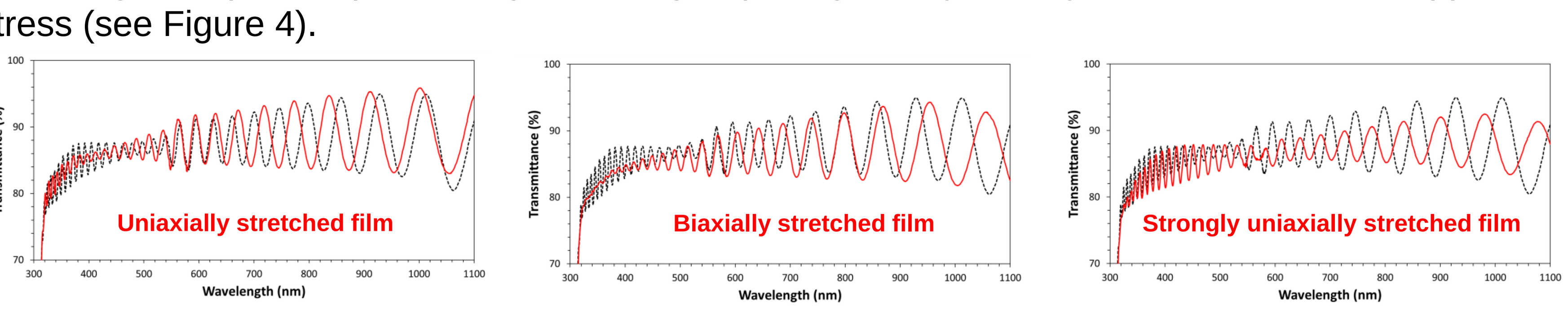


Fig. 4 – Shape and positioning of interferograms in the ultrathin PET film optical spectra are quite sensitive to the undergone mechanical deformation.

URBACH ENERGY CALCULATION

The Urbach plot is simply obtained by graphing the natural logarithm of optical absorption coefficient *vs.* photon energy (see Figure 5a). Linear regression analysis applied to the straight part in this plot has provided an Urbach energy (E_U) value of ca. 45.05 meV (see Figure 5b). E_U is a gauge of electronic disorder (amount of interstitial levels) in the solid polymer and in turn it provides information about structural disorder in the system. The experimentally found small E_U value suggests a low disorder content for the ultrathin PET film structure, which agrees with presence of crystallinity.

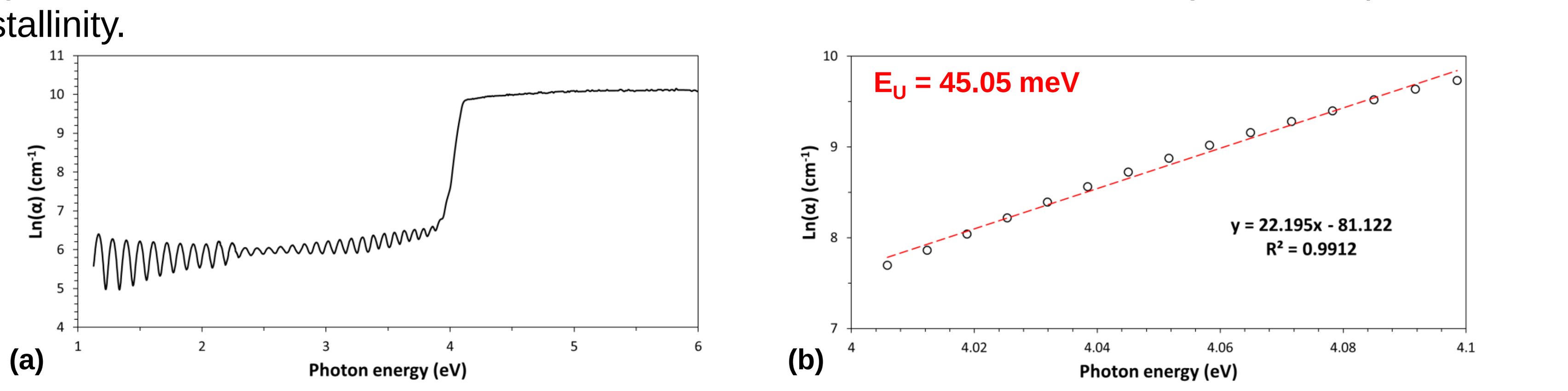


Fig. 5 - Urbach plot (a) and Urbach energy evaluation by linear regression analysis (b) for 'as received' ultrathin PET film.

The same type of analysis has been applied to slightly mechanically deformed (manually stretched) ultrathin PET film (see Figure 6a,b). Although, mechanical deformation had the effect to modify film thickness, the Urbach energy value remained practically unchanged (see Figure 6b). Therefore, structural disorder did not increase in this system as a result of the applied stress.

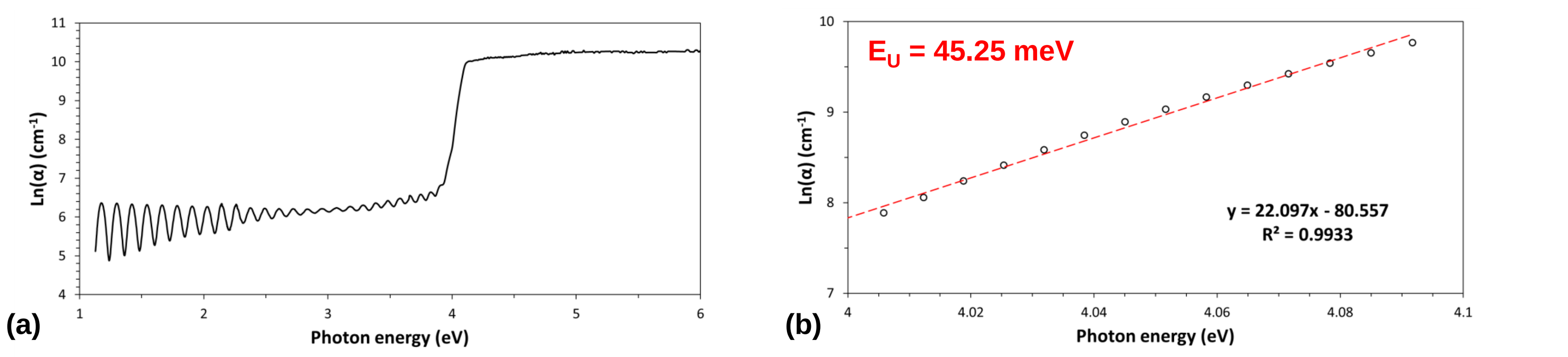


Fig. 6 - Urbach plot (a) and Urbach energy evaluation by linear regression analysis (b) for uniaxially stretched ultrathin PET film.

BANDGAP ENERGY AND ELECTRON TRANSITION MODEL

The Tauc plot method has been used to accurately measure the PET bandgap energy (E_g=3.96 eV). In addition, this approach has allowed to know the type of electron photoexcitation mechanism, which is active for this type of polymer. PET films were described by an **indirect allowed electron transition model** (other models failed), which involved thermalization, that is intraband electron transitions (see inset in Figure 7a). Such photoexcitation model agrees with the fluorescence phenomenon usually observed for PET (indeed, this material is used as plastic scintillator for ionizing radiations, like ultraviolet light, see Figure 2b).

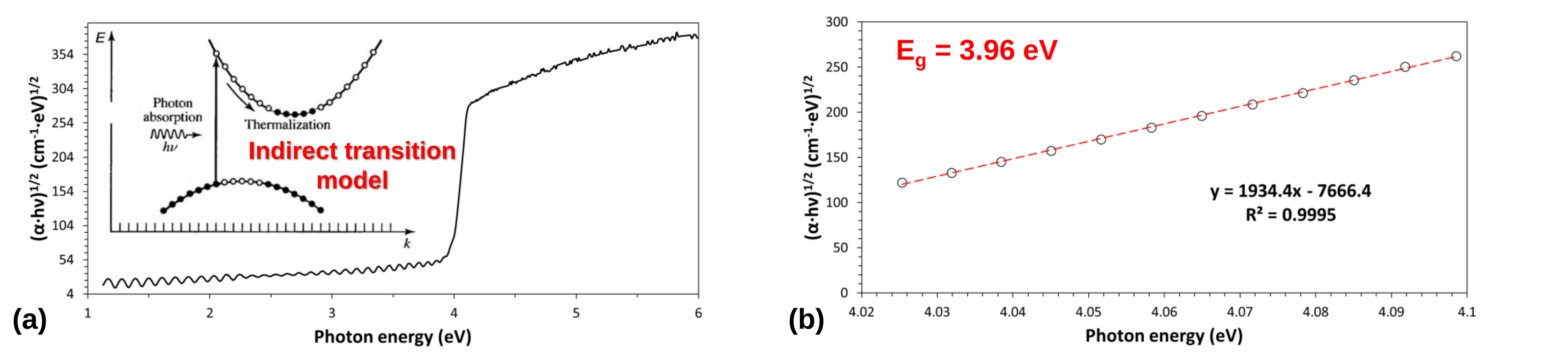


Fig. 7 – Tauc plot (a) and bandgap energy estimation by linear regression analysis (b) for 'as received' ultrathin PET film.

Manual stretching allowed to simulate mild uniaxial mechanical stresses that polymeric films suffer in service or during industrial uses. This investigation has shown that E_g is a polymer physical characteristic, which remains practically unchanged after mild mechanical stresses undergone by this material (see Figure 8b). Indeed, E_g depends mainly on atom types (composition) and the way in which atoms are chemically bonded together (constitution) in the repeating unit.

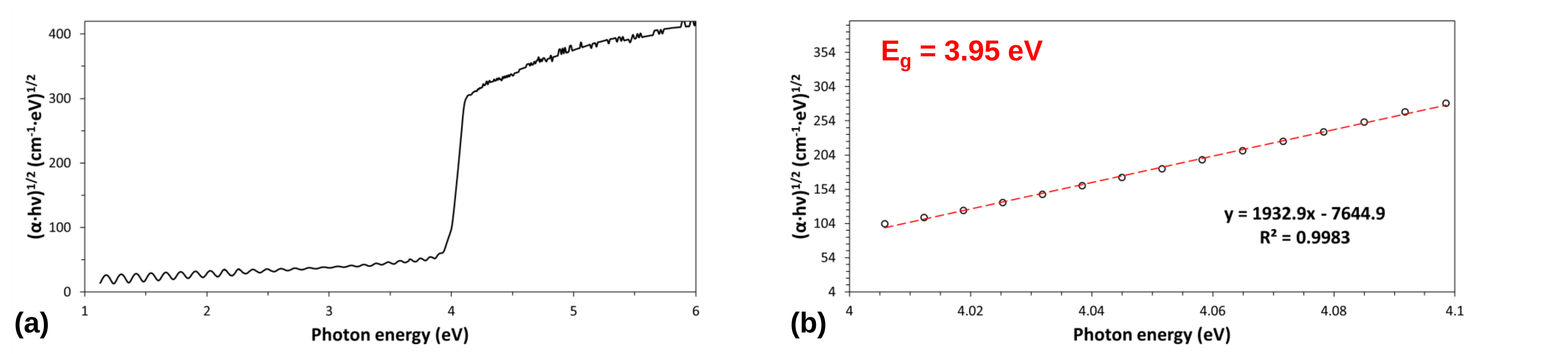


Fig. 8 – Tauc plot (a) and bandgap energy estimation by linear regression analysis (b) for uniaxially stretched ultrathin PET film.

POTENTIAL APPLICATION OF THE POLYMER BANDGAP ENEGY VALUE

According to the achieved experimental results, dielectric polymers like PET at solid-state have a band structure principally depending on the polymer chemical composition/constitution and only marginally on crystallinity, molecular weight and texture (i.e., fibrous/spherulitic morphology). Such behavior allows using the characteristic bandgap energy value to establish polymer nature. This approach can be conveniently adopted in fields like **microplastics** since these types of waste belong to only few different plastic classes that can be easily and with safety distinguished on the basis of the E_g parameter (identifying microplastics is an important aspect in this field, since it allows adequate selection of suitable recycling/elimination processes). Usually UV-Vis spectrophotometers have a very small beam spot (see Figure 9) and therefore sampling requires only little polymer amounts.

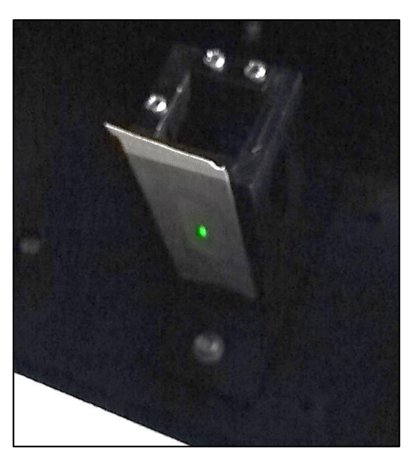


Fig. 9 – Very small beam spot (1-2mm) of the VWR, UV6300PC spectrophotometer.