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Extinction coefficient of free-standing chitosan films determined from partially coherent transmittance spectra

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ABSTRACT

The extinction coefficient (k) of free-standing chitosan-based films is determined in the spectral range 250–840 nm from normal incidence transmittance spectra showing partial coherence. Films of thicknesses (d) ranging between 3.7 and 20 μm casted from chitosan-acid acetic solutions are analyzed. Fast Fourier transform of oscillations in the transmittance spectra is used to determine film thicknesses by assuming normal dispersion in the refractive index (n) as reported in the literature. Transformation of partially coherent spectra to incoherent spectra was used to determine k which resulted of the order of 10^{-4}. The strength of anomalous dispersion in n introduced by an absorption band in k centered at wavelength 293 nm is analyzed within the framework of the Lorentz harmonic oscillator model. The reliability of the assumed dispersion of n, the determined k spectra and d values is tested by analyzing the experimental transmittance spectra with a theoretical model accounting for partial coherence. An inverse relationship between the degree of coherence and film thickness is found.

1. Introduction

Chitosan is a non-toxic, biocompatible, and biodegradable biopolymer obtained from the deacetylation of chitin. Chitin is a linear biopolymer formed by β(1 → 4) N-acetyl-D-glucosamine units found in the exoskeleton of crustaceans and fungi walls [1]. As a result of deacetylation, chitosan is mainly made of D-glucosamine moieties and it is soluble in a great variety of organic acids with the ability to form transparent, though, water insoluble, and flexible self-supporting films. It should be noted that a special treatment like crosslinking or neutralization including spontaneous neutralization [2], is necessary to achieve water insolubility of casted chitosan films prepared from acidic solutions. Chitosan has been proposed as a wet strength additive in paper for packing applications, nonwoven, fabric, fibers, biomedical, agricultural, and other uses [3–5]. More recently, optical applications of chitosan have emerged. For example, based on the humidity dependent swelling properties of chitosan, different configurations of interferometric humidity sensors have been proposed [6–8]. Furthermore, chitosan-based films have been used in planar optical waveguides for relative humidity sensors [9–12]. In the foregoing optical applications, the transparency of chitosan in the visible spectrum is exploited. As is known, the linear optical properties of materials are described by the complex refractive index $N = n + ik$ where n is the refractive index and k is the extinction coefficient. For transparent materials $n \gg k$ or $k = 0$ for practical purposes. Indeed, various authors have determined n of chitosan in thin film form by spectroscopic ellipsometry [13–16]. The differences among reported values of n are mostly due to specific processing conditions of chitosan samples, namely, source of chitosan, molecular weight, and deacetylation degree. However, the analysis of some refractive indices reported for chitosan has been summarized in a dispersion relation of the Sellmeir type valid for visible to near-ultraviolet wavelengths [17].

In the thin film regime optical spectra are characterized by interference fringes due to coherent superposition of electromagnetic waves. On a larger scale, interference effects are absent in the spectra of thick films due to the incoherent addition of multiple reflections. Often the transparency of chitosan-based composite thick films is qualitatively discussed in terms of the values of the transmittance (T) [18–20]. Such thick films could be adequate to determine the small values of k expected for chitosan, however, defects like unparallel surfaces, bubbles and/or not dissolved particles produce light scattering which complicates data analysis. Regarding optical absorption, it has been documented that chitosan-based thick films absorb in the near-ultraviolet range, showing a band at about wavelength $\lambda = 300$ nm [21–23]. In those works, absorption is discussed in terms of the absorbance spectra given by $A = -\log T$. However, for a better description of the linear optical response of chitosan and to potentialize optical applications, the fundamental parameter k, or equivalently, the absorption coefficient

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$\alpha = 4\pi k/\lambda$ should be determined. In between of the thin and thick film regimes is the one known as partially coherent which is by far less frequently found because its complexity.

In this work, we determine the extinction coefficient of free-standing chitosan films in the spectral range of 250–840 nm. The experimental details are presented in section 2. In section 3 the theoretical background to analyze coherent, incoherent, and partial coherent transmittance spectra is discussed. The results and discussion are presented in section 4 where film thicknesses and extinction coefficient are determined. The consistency of the procedure and reliability of results are further analyzed and confirmed by comparison of experimental data and calculations of partially coherent spectra. The concluding remarks are given in the last section.

2. Experimental

2.1. Casting of free-standing chitosan-based films

Chitosan of medium molecular weight, deacetylation degree of 75–85%, and viscosity 200–800 cps as specified by the supplier (Sigma Aldrich) was used as received. To obtain chitosan films 1 g of chitosan in a 1% (v/v) acetic acid solution was dissolved. Solution was left to stir overnight, then, it was filtrated to separate insoluble matter. Once filtration was done, volumes ranging from 2 to 7 ml in steps of 1 ml of the solution were poured into petri dishes of diameter 60 mm. Next, the films were obtained by drying at 60 °C for 16 h in a conventional oven.

2.2. Characterization techniques

Transmittance measurements at normal incidence were performed with a FilmTek 3000 equipment (Scientific Computing Inc.) in the wavelength range of 250–840 nm. The spectral measurements were performed at temperature 20 °C and relative humidity 45 ± 2% as measured with a RH/temperature SD datalogger (Sper Scientific). X-ray diffraction was used to characterize the structure of the films with a Rigaku Dmax/2100 system equipped with a Cu radiation (Kα = 0.15406 nm). The configuration geometry was parallel beam at fixed angle of incidence of 2°, scanning range was 2.5°–40° of 2θ with a step of 0.02° taken every 0.4 s. The chemical structure of the films was investigated with transmission Fourier transform infrared (FTIR) spectroscopy measurements, using a Spectrum GX system (Perkin-Elmer) in the range 4000–400 cm^{-1} with a resolution of 4 cm^{-1} and averaged over 24 scans.

3. Theoretical background

Let us consider a homogeneous film with complex refractive index $N = n + ik$ and thickness d embedded in a dielectric medium of refractive index $n_0 = 1$, as shown in Fig. 1. The incident electromagnetic wave experiences internal multiple reflections contributing to the transmittance spectrum which might be classified among one of three cases: i) coherent, ii) incoherent, iii) partially coherent.

3.1. Coherent case or wave optics limit

This case applies to *thin* films, that is, $d < 1$ μm for wavelengths in the ultraviolet–visible spectral range. By applying the wave optics formalism, the transmitted electromagnetic wave in Fig. 1 is obtained by the summation of the contributions (t_j) due to multiple reflections. Each t_j is given in terms of the Fresnel's complex coefficients at the interfaces r_{ij} and t_{ij}, and the phase shift in a round trip $\beta = 4\pi Nd/\lambda$. For example, $t_1 = t_{12}t_{21}e^{i\beta/2}$, $t_2 = t_{12}t_{21}r_{21}{}^2e^{i3\beta/2}$, and so on. Thus, the amplitude of the electric field of the transmitted electromagnetic wave corresponds to the superposition of an infinite number of terms which can be expressed in closed form. The transmittance (T_{WO}) is obtained by taking the product of such summation with its complex conjugate

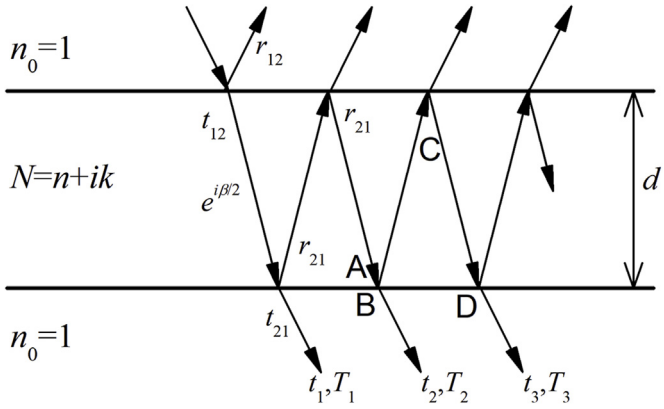

Fig. 1. Multiple internal reflections in a free-standing film of thickness d and complex refractive index N embedded in air. Depending on the case, coherent or incoherent, the summations of contributions is performed, respectively, with electric field amplitudes (t_j) or intensities (T_j). The phase shift for a single pass through the film is exp ($i\beta/2$).

leading to [24],

$$T_{WO} = \left| \frac{(1 - r_{21}^2)\exp(i\beta/2)}{1 - r_{21}^2\exp(i\beta)} \right|^2 , \quad (1)$$

where the Fresnel relationship $t_{12}t_{21} = 1\text{-}\ r_{21}{}^2$ has been used and at normal incidence, $r_{21} = (N\text{-}1)/(N+1)$. Thus, a typical transmittance spectrum shows interference fringes due to the oscillatory term in the denominator of Eq. (1). From Eq. (1), for a non-absorbing film ($k = 0$) the fringes of transmittance reach the maximum value (100%) at wavelengths where $\beta = 2m\pi$ where m is an integer. Methods to determine the optical constants of films from coherent transmittance spectra are well known [24,25].

3.2. Incoherent case or geometric optics limit

This case corresponds to *thick* films $d \gg \lambda$ (geometric optics regime) which commonly applies to substrates [26,27]. Referring to Fig. 1, the sum is performed by adding the contributions of intensities (T_j), considering the exponential decay due to absorption as the beam travels across the film $e^{-\alpha d}$, transmittance at interfaces $(1\text{-}|r_{21}|^2)$, and internal reflections (each of magnitude $|r_{21}|^2$). For example, $T_1 = (1\text{-}|r_{21}|^2)^2e^{-\alpha d}$, $T_2 = (1\text{-}|r_{21}|^2)^2|r_{21}|^4e^{-3\alpha d}$, and so on. The fact that irradiances rather than electric field amplitudes are considered is termed incoherent because any phase relationship between the different contributions is eliminated and interference effects are absent at all. The transmittance spectrum for the incoherent case is given by Ref. [26],

$$T_{GO} = \frac{(1 - |r_{21}|^2)^2\exp(-\alpha d)}{1 - |r_{21}|^4\exp(-2\alpha d)} . \quad (2)$$

From Eq. (2) it is possible to calculate the absorption coefficient in terms of the transmittance T_{GO} and the reflectivity $|r_{21}|^2$ of the air-film interface as,

$$\alpha = \frac{1}{d}\ln\left[\frac{(1 - |r_{21}|^2)^2 + \sqrt{(1 - |r_{21}|^2)^4 + 4T_{GO}^2|r_{21}|^4}}{2T_{GO}}\right] , \quad (3)$$

Then, k is determined according the relationship $\alpha = 4\pi k/\lambda$ and n from inverting the expression for $|r_{21}|^2$. This procedure has been largely applied to determine the optical constants of materials in thick film form (slabs) from normal incidence measurements. A comprehensive discussion on this procedure and its misuse can be found in Ref. [27].

3.3. Partially coherent transmittance spectra

Sometimes the transmittance spectra of transparent films show