Optical and thermal techniques combined for a better characterization of hydrogels

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Abstract

In this paper, we aim to evaluate chemically and optically, three types of hydrogels. Thus, the phase transitions that take place during the water-polymer interaction, present in hydrogels by thermal analysis techniques, namely differential dynamic calorimetry (DSC) will be studied. These studies will be correlated with experimental results obtained by optical methods (spectroscopy in the field of THz) and will lead to a better understanding of the specific properties of hydrogels for medical applications. In this collaboration on the study of hydrogels by optical and chemical methods, we aim to deepen research in the field of development of new hydrogels with medical applications, obtained by processing with ionizing radiation and understanding the structure-properties relationship of these materials.

We thus determined the different types of phase transitions of the water absorbed in a polymeric material; the experimental data obtained will lead to the understanding of the structural properties that define a material in the form of a hydrogel; it will be possible to evaluate the interaction mechanisms of water-polymer-active principles with a role in the accelerated healing of some skin wounds. From an optical and spectroscopic point of view, hydrogels were studied in the THz domain, by obtaining transmission spectra and refractive indices, in the 0.1-3THz frequency range, using the THz-TDS spectroscopic kit (THz-time domain spectroscopy).

Our experimental set-up it is a THz-TDS system (an Ekspla THz kit with a FemtoFiber® laser produced by TOPTICA)- fig 1. The system can measure a transmission spectrum in the THz domain (0.2- 4.5THz), by measuring the signal detected synchronously with a lock-in amplifier. The phase shift, for the synchronous detection, is introduced by the delay line from the emitter arm.

The TDS kit system has a sample holder in the middle of the active area where is focused the THz beam with the two lenses (L5 and L6 with a focal length of 50mm each) to allow the use of the maximum density of the THz emitted radiation.

All our samples were measured in the same holder, made from MD polyethylene, which ensures a uniform sheet of the studied material.

We have also installed close to the center of the system an iris diaphragm (not represented in fig.1.) to avoid the backscattering or parasite reflections of the radiation and to control the THz beam dimension.

The spectroscopic system has a software (THz Spectrometer.vi) virtual instrument done in Lab VIEW programs that command the entire system: it makes the necessary settings of the system and for recording parameters, and records the transmission spectrum on the entire domain (0.2 – 4.5) THz or in part of it, with the necessary resolution. The program can measure the spectrum and it can save in ASCII format the results.

The sample's transmission spectra show the calculated sample transmission spectra, obtained by dividing measured spectra to reference spectra.
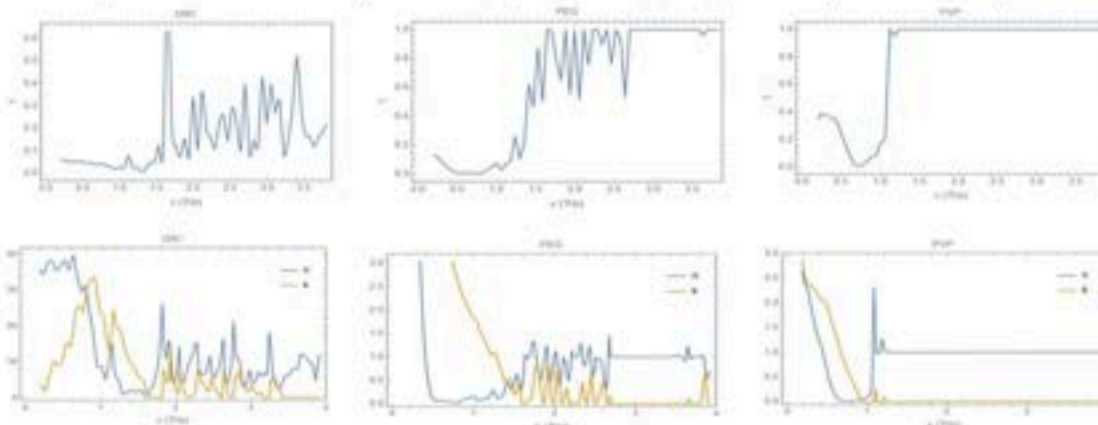
Kramers-Kronig dispersion relations

The refractive index n and the extinction coefficient k (optical constants) may be calculated using the Kramers-Kronig dispersion relations [1]:

$$n = \frac{1-r^2}{1+r^2-2r\cos\theta}, \tag{1.a}$$

$$k = \frac{-2r\sin\theta}{1+r^2-2r\cos\theta}, \tag{1.b}$$

where θ is the phase difference between the incident and reflected waves and has the form

$$\theta(\omega_i) = \frac{2\omega_i}{\pi}\int_0^\infty \frac{\ln[r(\omega)]-\ln[r(\omega_i)]}{\omega^2-\omega_i^2}\,d\omega, \tag{2}$$

and $r=R^{1/2}$ is a positive real number, the square root of reflectance R at normal incidence. The integral from Eq. (2) is evaluated numerically. Eqs. (1) are relations that express the optical constants as functions of the reflectance over the entire spectrum. They express an exact relation between the real and the imaginary part of the dielectric constant $\varepsilon=(n-i\,k)^2$. They may be derived as a direct consequence of the causality principle and the fact that the dielectric must be an analytically continuous function of the complex frequency [2]. The limits of the integration should be the extremities of the spectrum where the reflection approaches constant value. However, in practice we often do not have a full spectrum. In this case various approaches may be used to compensate for the lack of the wings. But according to [3] the contribution of the wings to the integral from Eq. (2) should cancel each other. In this work we chose this most simple of approaches. Furthermore, we neglected the multiple reflections inside the layer and we used the approximation $r^2=1-T$. Our measurement system was of such nature that we could measure only T.