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DETERMINATION OF OPTICAL CONSTANTS OF POLYMER FILMS THROUGH REFLECTION

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Abstract:
The transmittance values measured in IR specular external reflection (RS) or internal reflection (ATR) spectra can be used to determine the optical constants of solid surfaces or dielectric films laid on solid substrates.
To obtain the optical constants of polystyrene films laid on steel we used Kramers-Kronig analysis. In this case, the optical constants are obtained from IR external reflection spectrum recorded at a single incidence angle. The transmittance measured and the phase shift angle obtained by Kramers-Kronig integral, are used in this case.
Using Kramers-Kronig analysis offers the advantage of processing a large volume of data.
Keywords:
Reflection-absorption, optical constants, IR spectra, Kramers-Kronig analysis, dispersion analysis

1. INTRODUCTION

The study of reflectance spectra of films deposited on solid surfaces allows the determination of thickness and optical constants of these: refractive index n and absorption index k.

In order to determine the optical constants of polymer films one can use the specular external reflectance spectra or the internal reflectance spectra. If the polymer film deposited on the metal is thick, it can be treated as a bulk material. The reflectance spectrum recorded is not influenced by the substrate.

The reflection and transmission of radiation on solid surfaces are expressed by the complex reflection coefficient $\tilde{r} = |\tilde{r}| \exp(i\theta)$ and the complex transmission coefficient $\tilde{t} = |\tilde{t}| \exp(i\theta)$. They depend on the complex refractive index of the film $\tilde{n} = n - ik$ and on the angle of incidence.

Reflectance, denoted by R represents the ratio of the reflected radiation intensity I_r and the incident radiation intensity I_o and it is equal to the square complex reflection coefficient: $R = r^2 = |\tilde{r}|^2$.

Transmittance, denoted by T represents the ratio of the transmitted radiation intensity I_t and the incident radiation intensity I_o and is equal to the square complex transmission coefficient: $T = t^2 = |\tilde{t}|^2$.

For thick films (with thickness higher than 50 μm), the optical constants are determined from the specular reflectance spectra (RS) or from the attenuated total reflectance spectra (ATR). You can use the reflectances R1 and R2 measured at two angles of incidence or the reflectance R at one angle of incidence and θ angle measured across the whole spectral domain [4,8,14]. This is possible by Kramers-Kronig analysis, using integral:

$$\theta(\nu_i) = \frac{\nu_i}{\pi} \int_0^\infty \frac{\ln R(\nu)}{\nu^2 - \nu_i^2} d\nu \qquad (1)$$

From reflectance R and angle θ, the complex refractive index is determined, for normal incidence:

$$\tilde{n} = n - ik = \frac{(1-R) - i \cdot 2\sqrt{R} \sin\theta}{1 + R - 2\sqrt{R} \cos\theta} \qquad (2)$$

In case of specular reflection from the polymer thin films deposited on metals (with thickness less than 10 μm), the reflected radiation contains two components: one reflected from the air-film interface (I_r intensity) and one reflected by the film-metal interface (I_t intensity), after having crossed twice the polymer film, as shown in Figure 1.

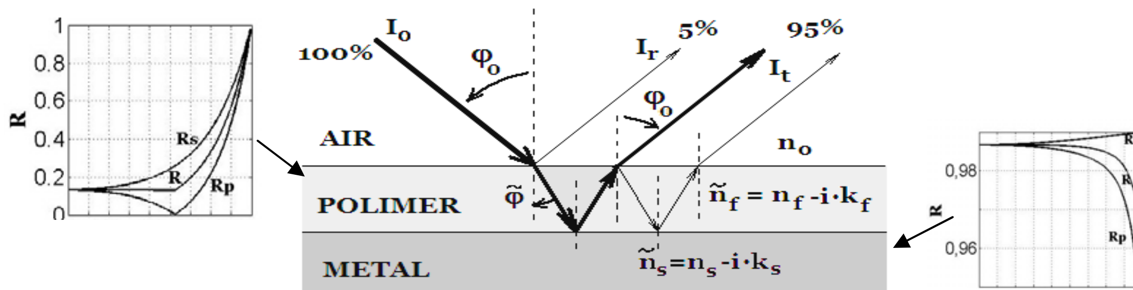

Figure 1. The specular reflection of radiation for thin films deposited on metals

The reflectance due to reflection at the air/film interface is about 5% since the refractive indices of polymers is less than 1.5 in the middle-IR spectral domain. The reflection at the polymer/metal interface is much higher and the reflectance is about 99%. The radiation reflected from the polymer/metal interface and crossing twice the polymer film is thus about 95% of the incident radiation intensity. It is almost 20 times more intense than the reflected beam to the air/polymer interface. For this reason, this spectrum is a reflection-absorption spectrum (or a transflectance spectrum). It is similar in terms of quality to the transmission spectrum of the polymer film.

This spectrum can be processed to obtain optical constants n and k [9].

It is necessary to know the transmittance $T(\nu)$ along the whole spectral domain and by means of the Kramers-Kronig relationship the θ angle is determined [12.13].

$$\theta(\nu) + 2m\pi = -\frac{\nu}{\pi} P \int_0^{\infty} \frac{\ln T(\nu')}{\nu'^2 - \nu^2} d\nu' + 2\pi\nu d \quad (3)$$

Transmittance T and θ angle are related to the complex refractive index by the relationship:

$$\sqrt{T} e^{i\theta} = \frac{4\tilde{n}}{(\tilde{n}+1)^2 e^{-i\delta} - (\tilde{n}-1)^2 e^{i\delta}} \quad (4)$$

where: $\delta = 2\pi\nu\tilde{n}d_f / c$ depends on the thickness d_f of the film [3].

Dispersion analysis is another way of obtaining the optical constants of thin films deposited on metal surfaces. This method can be more flexible than the Kramers-Kronig relations as it can be applied to a more complicated geometry.

Dispersion analysis is based on building an appropriate model for calculating the dielectric and optical properties of this model. The best known is the Drude-Lorentz damped harmonic oscillator model [11] for the complex dielectric function:

$$\varepsilon(\nu) = \varepsilon_\infty + \sum_j \frac{\nu_{pj}^2}{\nu_{oj}^2 - \nu^2 - i\gamma_j \nu} \quad (5)$$

It describes the optical response of a set of harmonic (damped) oscillators. Here ε_∞ is the so-called "high-frequency dielectric constant", which represents the contribution of all oscillators at very high frequencies. Parameters ν_{pj}, ν_{oj} and γ_j are the "plasma" frequency, the transverse frequency (eigenfrequency) and the linewidth (scattering rate) respectively of the j -th Lorentz oscillator. Reflectance R or transmittance T can be obtained from the theoretical model of the complex dielectric function. The spectra of these optical magnitudes are compared to those experimentally determined. The model parameters are continuously adjusted to fit the theoretical values with the experimental data measured. For the reflection-absorption spectra, the theoretical transmittance and the experimental transmittance are compared. When the differences between the theoretical and experimental spectra are minimal, the parameters fitting process is stopped.

Suppose, we have a set of N experimental data points $\{x_j, y_j, \sigma_j\}$ (j = 1,...., N), that we want to fit. Here, x_j is the data coordinate, y_j is the data value and σ_j is the data error bar. Next, we take a model, which calculates the model value $y = f(x, p1,...., p_M)$ for a set of M internal parameters.

So-called Levenberg-Marquardt algorithm is used to minimize the amount

$$\chi^2 = \sum_j^N \left(\frac{y_j - f(x_j, p_j....p_M)}{\sigma_j} \right)^2 = \chi^2(p_1,....p_M) \quad (6)$$

is used.

The fitting process stops when the stopping criterion is fulfilled [10].

In the case of the internal reflection at angles of incidence greater than the critical angle, the radiation is totally reflected on the surface film. The evanescent-wave penetrates into the superficial thin film. The depth of radiation penetration into the superficial film is given by the relationship:

$$d_p = \frac{\lambda}{2\pi\sqrt{n_o^2 \sin^2 \varphi_o - n_f^2}} \tag{7}$$

The depth of penetration is a measure of how far radiation penetrates into the sample in an ATR experiment, calculated as the depth at which the electric field of the evanescent wave has decreased to 37% of its original value.

Figure 2 presents the model of the internal reflection on thin films (with thickness d_f less than the depth of penetration d_p) deposited on metal mirrors.

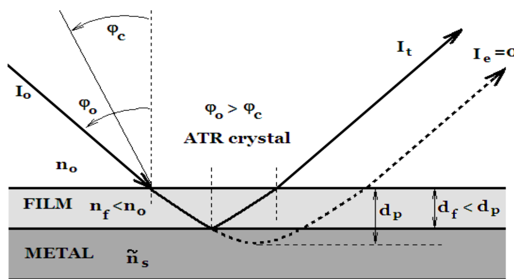

Figure 2. The attenuated total reflection from thin film deposited on metal surface

The radiation that penetrates through the polymer film as well as an evanescent wave, is reflected on the polymer/metal interface and it crosses the polymer film again. In this case, the internal reflectance spectra of thin films resemble more the transmission spectra and have a much different aspect, as compared to those recorded for thick films [4,6]. In the case of thin film, absorption bands are not displaced or distorted, if the incidence angle is close to the limit. The spectrum recorded is influenced by the nature of the substrate.

In order to determine the thickness of the surface films, one may use only the external reflectance spectra. For this, it is necessary that the film should have even thickness and that it should have values comparable to the wavelength of the radiation. Interference fringes may occur between the radiation reflected from the interface air/film and one that reflects the film/metal interface and crossing the film 2 times. The interference fringes are missing in case of internal reflection [4].

2. EXPERIMENTS

Thin films of polystyrene (PS) were obtained by depositing a solution of polymer dissolved in toluene on the surface of OLC-35 steel. Reducing the solvent evaporation rate allows us to obtain a film with an even thickness. The low concentration of polymer in the solvent allowed us to obtain thin films with thickness less than 1μm. Then, the metal sample coated with polymer was heated to 500°C, in order to evaporate all traces of solvent. The metallic surfaces used as substrates were obtained by grinding and polishing. IR reflectance spectra were recorded using the specular reflection device of the UR-20 spectrograph. In order to obtain the optical constants of the polymer film, the reflection-absorption spectra were processed using the RefFIT software [10].

3. RESULTS AND DISCUSSION

The IR reflection-absorption spectra recorded at incidence angles of 20 and 55 degrees are shown in Figure 3. The diagram shows the spectral ranges 500-850 cm^{-1} and 2400-3360 cm^{-1}, which contain absorption bands corresponding to the C-H stretching vibrations of aromatic nucleus [2].

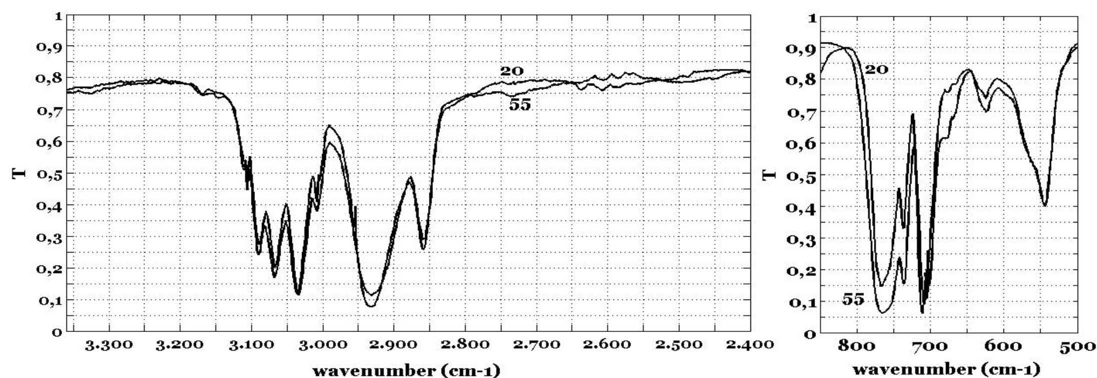

Figure 3. The reflection-absorption spectrum of polystyrene deposited on steel, recorded for 20 and 55 degrees angles of incidence

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It is noted that changing the angle of incidence does not alter significantly the transmission spectrum of polystyrene. Reflectance R and transmittance T depend very little on the incidence angle, as can be observed in Figure 1.

Because the thickness of the superficial film is less than 1μm, the interference fringes are not present in the recorded spectra. For the same reason the recorded spectrum is a reflection-absorption (transflection) one.

The spectrum obtained can be processed to obtain the optical constants n (refractive index) and k (absorption index).

In order to improve the accuracy of the dielectric function, both R-A spectra recorded at incidence angles of 20 and 55 degrees were simultaneously fit. We also used the refractive index of polystyrene n_f = 1.57 ellipsometrically determined for λ = 562.5 nm [7] and the value n_f = 1.5842 for λ = 633 nm [1].

The refractive index spectrum obtained by dispersion analysis of reflection-absorption spectrum for polystyrene deposited on steel is shown in Figure 4.

Absorption index k has a spectrum very similar to the absorption spectrum. The values of the absorption coefficient are low so that it can be concluded that polystyrene is almost transparent and in the IR range. In this spectrum the positions of the absorption bands do not show deviations from the positions of the absorption bands in the reflection-absorption spectrum. It can also be noticed that the intensity of absorption bands decreases at higher frequencies. The wavenumbers corresponding to the model used are about 5 cm^{-1} higher than those of literature [2].

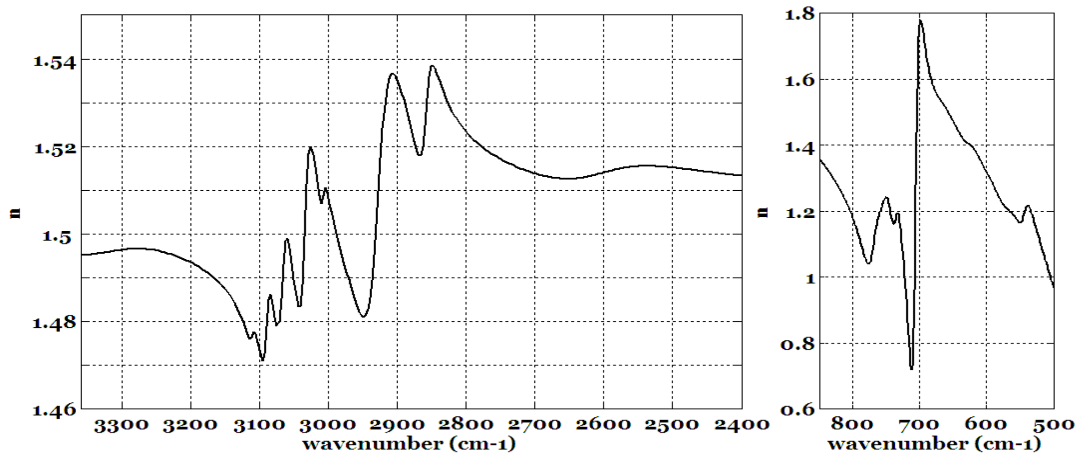

Figure 4. The refractive index spectrum for polystyrene deposited on steel

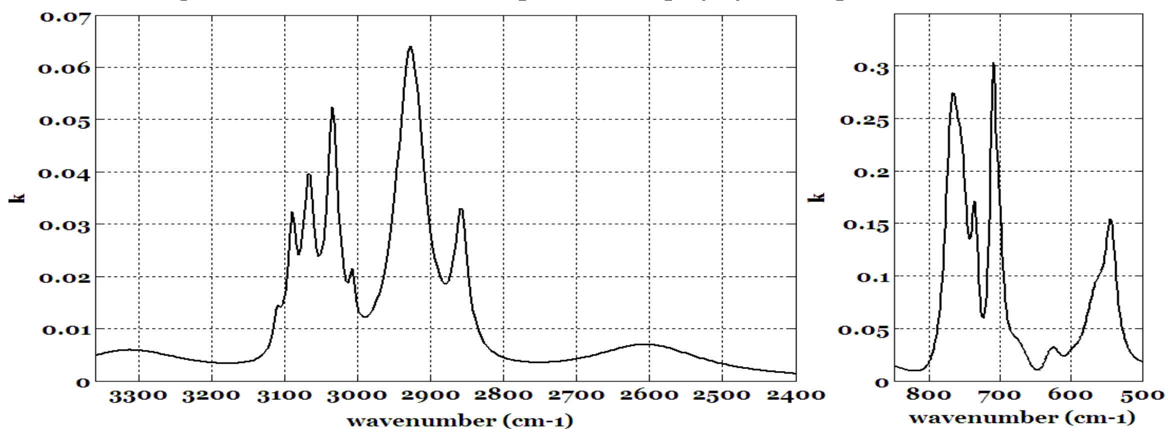

Figure 5. The absorption index (extinction coefficient k) spectrum for polystyrene deposited on steel

4. CONCLUSIONS

The IR reflectance spectra for thin films (with thickness less than 1μm) are reflection-absorption spectra in which transmittance T is recorded. The reflection-absorption spectrum for polymer films is very similar in terms of quality to the transmission spectrum.

The dispersion analysis of the reflection-absorption spectra is more accurate and easier than the Kramers-Kronig analysis. Kramers-Kronig analysis is used mainly for superficial thick films or for bulk material.

Simultaneous fitting of several datasets of different types related to the superficial film leads to obtaining correct values for optical constants **n** and **k**.

The internal reflectance spectra for thin films, deposited on metals, with thickness less than the depth of penetration at angles of incidence greater than the critical angle are the reflection-absorption spectra and not the attenuated total reflectance spectra. They have the same look as the transmission spectra and can be used to determine the optical constants of the superficial film.

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