



Simion Jitian

Determination of Optical Constants of Polystyrene Films from IR Reflection-Absorption Spectra

Determination of The transmittance values measured in IR reflection-absorption (RA) spectra were used to determine the optical constants of dielectric films laid on solid substrates. In order to obtain the optical constants of polystyrene films laid on steel we used dispersion analysis. In this case, the optical constants are obtained from IR spectrum recorded at a single incidence angle. The use of dispersion analysis offers the advantage of processing a large volume of data.

Keywords: *reflexion-absorption, optical constants, IR spectra, dispersion analysis*

1. Introduction

Polystyrene (PS) films deposited on solid substrates are used in various areas of science and technology, including optical mechanical industry [1]. The determination of optical constants of the polymer is important for various optical applications. Optical properties of the polymer are very sensitive to its various transformations during the oxidation or degradation processes.

Reference literature describes several methods of obtaining the optical constants of PS. The transmission spectra, specular external reflection spectra or internal reflection spectra can be used to determine the optical constants of polymer films. The Kramers-Kronig analysis for processing of these spectra is frequently used.

To obtain the optical constants spectra: $n = f(\nu)$ and $k = f(\nu)$ we use dispersion analysis, a much simpler method than the Kramers-Kronig analysis. It is commonly used to process the recorded spectra at a single incidence angle. The method we have used leads to obtaining better results than the Kramers-Kronig analysis, especially when spectra containing many absorption bands, such as PS spectrum, are processed.

In the case of specular reflection on polymer thin films (with thicknesses less than 20 μm) deposited on metals, the reflected radiation contains two

components: one reflected from the air-film interface and one reflected by the film-metal interface, after it traversed the polymer film twice.

The reflectance due to reflection at the air-film interface has values of about 5% because the values of the polymers refractive index in IR are less than 1.6. In this case the reflectance at the polymer-metal interface has values exceeding 99%. The intensity of radiation reflected at the polymer-metal interface that crosses twice the polymer film is thus about 95% of the incident beam intensity, being almost 20 times more intense than the beam directly reflected at the air-polymer interface. For this reason, this spectrum is a reflection-absorption (or transfective) one and is qualitatively similar to the polymer film transmission spectrum. This spectrum can be processed to obtain optical constants n and k corresponding to complex refractive index [2].

Dispersion analysis is based on building an appropriate model for dielectric function and calculating the optical properties corresponding to this model. The best known model is Drude-Lorentz [3, 4] which defines the electric permittivity:

$$\varepsilon(\nu) = \varepsilon_{\infty} + \sum_j \frac{\nu_{pj}^2}{\nu_{0j}^2 - \nu^2 - i\gamma_j\nu}. \quad (1)$$

It describes the optical response of a set of harmonic (damped) oscillators. In this relation, ε_{∞} is so-called "high-frequency dielectric constant", which represents the contribution of all oscillators at very high frequencies (compared to the frequency range under consideration). The parameters ν_{pj} , ν_{0j} and γ_j are the "plasma" frequency, the transverse frequency (eigen-frequency), and the line-width (scattering rate), respectively of the j -th Lorentz oscillator. For the proposed model, from the permittivity, we can calculate all optical variables such as reflectance R and transmittance T . The spectrum of these theoretically calculated quantities is compared with those experimentally determined.

Suppose, we have a set of N experimental data points in the recorded transmission spectrum $\{T_j, \nu_j, \sigma_j\}$ ($j = 1, \dots, N$) that we want to fit. Here, ν_j is the light frequency, T_j is the transmittance value, and σ_j is the data error bar. For a set of M internal parameters, the values $T = f(\nu, p_1, \dots, p_M)$ are calculated based on the model.

The so-called Levenberg-Marquardt algorithm is used to minimize the value:

$$\chi^2 = \sum_{j=1}^N \left(\frac{T_j - f(\nu_j, p_1, \dots, p_M)}{\sigma_j} \right)^2 = \chi^2(p_1, \dots, p_M). \quad (2)$$

The fitting process stops when the stopping criterion is met [5].

If the surface film is thin, with thickness between 1 μm and 100 μm and it is absorbent ($k \neq 0$), then the interference fringes appeared in the IR spectrum.

The dispersion analysis allows to determine the surface film thickness d_f if we introduce in the fitting process d_f as an additional experimental parameter. This affects the obtained values of the refractive and absorption indexes [5].

2. Experimental

Thin films of polystyrene (PS) were obtained by depositing a solution of polymer dissolved in chloroform on the surface of a copper metal samples. A copper metal mirror was chosen as a substrate of polystyrene film because the copper has high reflectance values ($1 > R > 0.99$) in the IR spectral range investigated. To obtain a surface film with uniform thickness we decreased the evaporation rate of the solvent. After solvent evaporation, polymer-coated metal sample was maintained for 2 hours in a vacuum chamber at a pressure of 10^{-1} torr and temperature 120°C to evaporate traces of solvent. The metal surface used as substrate for the polymer film was obtained by grinding and polishing.

For the polystyrene film deposited on the copper mirror surface, reflection-absorption spectrum (RA) at 20° incidence angle was recorded. The IR reflection-absorption spectra were recorded using a specular reflectance device of UR-20 Carl Zeiss Jena spectrophotometer. In order to obtain optical constants of polymer film, reflection-absorption spectra were processed using ReFFIT program [5].

After recording the reflection-absorption spectrum, the polystyrene film deposited on copper was detached from the metallic mirror surface. For the polystyrene film detached, the transmission spectrum at normal incidence was recorded, with UR-20 spectrograph.

3. Results and discussion

The IR reflection-absorption spectrum of the PS film deposited on copper, recorded at 20° incidence angle is shown in the Figure 1. In this figure the transmission spectrum of the same PS film who was detached from the copper surface is shown. In both spectra the transmittance T varies with the frequency.

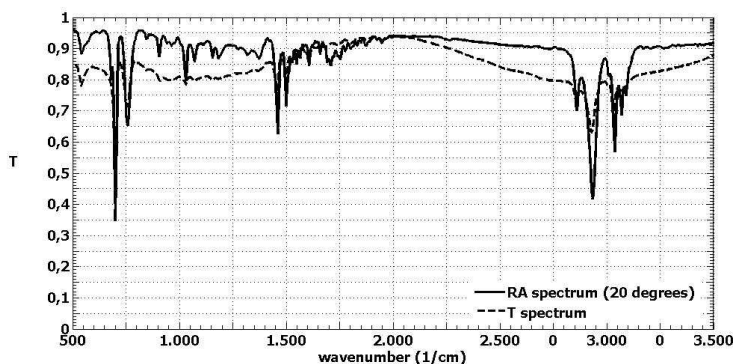


Figure 1. The spectra of a polystyrene film: transmission (T) and reflection-absorption (RA) recorded at 20° incidence angle

The most intense bands correspond to ν CH stretching vibrations in the mono-substituted aromatic cycle and ν CH₂. Other characteristic bands of polystyrene are those at 1070 and 1028 cm^{-1} that correspond to bending vibrations (in the plane) of hydrogen atoms from mono-substituted cycles of as well as to γ CH bending vibration (out of plane) corresponding to hydrogen atoms in mono-substituted aromatic cycle at 760 to 700 cm^{-1} [6].

For incidence angles smaller than 50° the values of reflectance R and transmittance T depend slightly on the angle of incidence. For this reason, the reflection-absorption spectra recorded at 20° incidence angle are very similar to the transmission spectrum at normal incidence.

The experimental spectra of the PS film can be processed in order to obtain optical constants of the polymer: n and k. To improve the accuracy of the dielectric function were used simultaneously in the fitting process the reflection-absorption spectrum recorded at 20° incidence angle and the refractive index of PS, in the visible spectrum, from the literature [7]. The processed RA spectrum contains a set of 621 experimental points, in digitized form and refractive index spectrum of PS from the visible contain a set of 374 pairs of values (n, ν). The transmission T spectrum contains a set of 911 experimental points, in digitized form.

The theoretical spectrum which corresponds to Drude-Lorentz model of dielectric function was obtained from the dispersion analysis of the experimental spectrum using computer program RefFIT. The theoretical transmission spectrum corresponding to the physical model that best approximates the experimental transmission spectrum is shown in Figure 2.

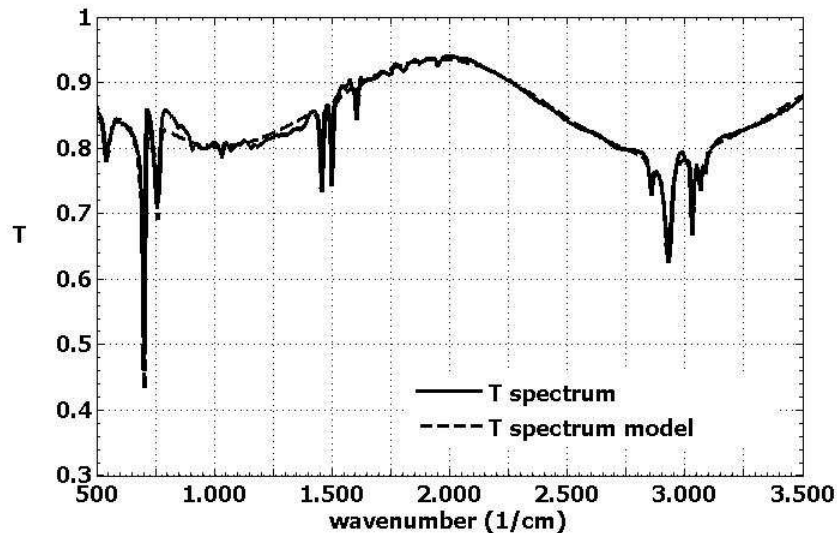


Figure 2. The spectra of a PS film: transmission and RefFIT model

The RefFIT program used for the dispersion analysis of the reflection-absorption spectrum of PS allows the spectra to be processed, which shows the interference fringes. In this case, the film thickness is used as an experimental variable parameter in fitting process. For the model of dielectric function we used 124 internal parameters. These parameters correspond to a set of 41 damped harmonic oscillators and "high-frequency dielectric constant". The model internal parameters and the experimental parameter are continuously adjusted to fit the theoretical values with experimentally measured data. In case of reflection-absorption spectra the theoretical transmittance and experimental transmittance spectra are compared. The parameter fitting process stops when the differences between theoretical and experimental spectra are minimal.

The film thickness was additionally introduced as experimental parameter. This spectrum shows weak interference fringes corresponding to a 27.56 μm thick film deposited on metallic mirror surface.

The refractive index spectra $n=f(\nu)$ obtained by the dispersion analysis of the reflection-absorption and transmission spectra of PS film deposited on copper are shown in Figure 3.

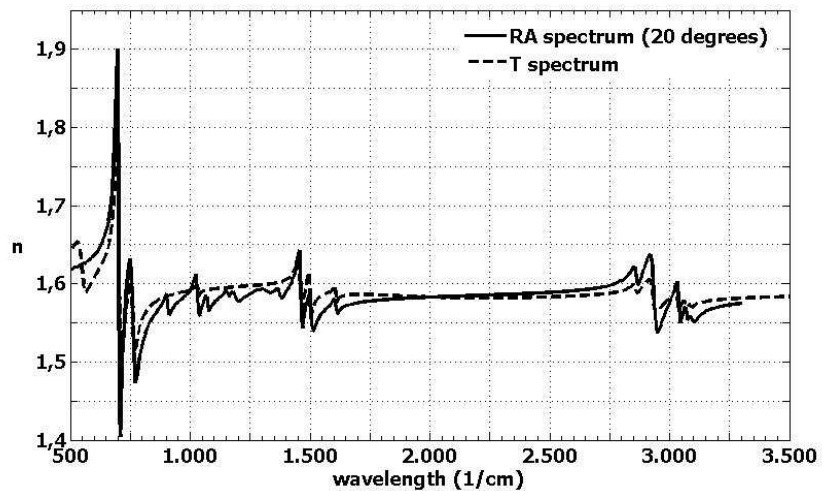


Figure 3. The refractive index spectra obtained by dispersion analysis of the RA and T spectra for PS thin film deposited on copper

The absorption index k has a spectrum very similar to the absorption spectrum. The absorption index spectra of PS thin film deposited on copper $k=f(\nu)$ are shown in Figure 4.

Similar data have been obtained by other authors by processing the ATR-IR spectra or the transmission spectra [1, 7]. Other authors have studied PS films by Kramers-Kronig analysis of the specular reflection spectra [2] or by interpretation of the spectro-ellipsometry measurements [8].

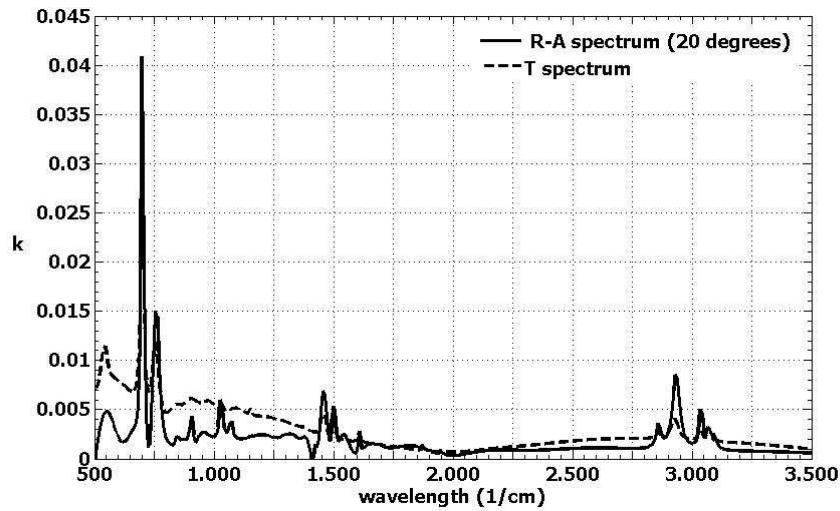


Figure 4. The absorption index spectra obtained by dispersion analysis of the RA and T spectra for PS thin film deposited on copper

Main frequencies of absorption bands of PS spectrum obtained by dispersion analysis of the reflection-absorption and transmission spectra were presented in Table 1 and compared with those given in the literature [1,6].

It is noted that in general the spectral bands in the experimental reflection-absorption spectrum are slightly shifted to higher frequencies than those in the literature, which correspond to the transmission spectrum. Such shifts, or changes in the absorption bands have been reported by others authors [1,9]. These shifts were assigned to the influence of the refractive index on the reflectivity, coupled with the significant changes in refractive index in the region of the anomalous dispersion. Distortion or displacement of absorption bands can be produced due to the existence of the interference fringes [2].

Table 1.

Assign- ment	Inten- sity	Transmission spectrum (literature)			R-A spectrum (experimental)		T spectrum (experimental)	
		[6]	[1]		ν_0 cm ⁻¹	k -	ν_0 cm ⁻¹	k -
		ν_0 cm ⁻¹	ν_0 cm ⁻¹	k -				
	medium	3083	3082	0.010	3091	0.02	3088	0.01
vC-H aromatic	intense	3061	3060	0.014	3069	0.03	3066	0.02
	intense	3029	3026.5	0.024	3037	0.06	3032	0.04
$\nu_{\text{sim}}\text{CH}_2$	very intense	2923	2923	0.029	2933	0.11	2929	0.05
	medium	2851	2849.5	0.011	2860	0.03	2858	0.02
vC-C aromatic	medium	1602	1601.5	0.022	1607	0.02	1606	0.04
	intense	1493	1493	0.041	1502	0.06	1499	0.07
CH ₂ + C=C	very intense	1450	1451.5	0.045	1460	0.10	1457	0.06
δCH_2	medium	1376	1371.5	0.011	1370	0.01		
vibration cycle	medium	1182	1181.5	0.009	1186	0.02		
vibration cycle	medium	1154	1154.5	0.009	1156	0.01		
vibration cycle	medium	1070	1069.5	0.014	1071	0.03		
vibration cycle	intense	1028	1028	0.024	1030	0.05	1032	0.02
C-H	medium	907	906.5	0.017	906	0.02	910	
$\gamma\text{C-H}$	very intense	760	756.5	0.095	760	0.17	759	0.11
vibration cycle	very intense	700	700	0.117	701	0.39	702	0.39
	intense	538	540.5	0.066			547	0.07

4. Conclusions

The IR reflection spectra of thin films (with thickness less than 20 μm) are reflection-absorption spectra for which the recorded size is transmittance. The appearance of reflection-absorption spectra is very similar in the terms of quality, to the transmission spectrum of the polymer.

The dispersion analysis of reflection-absorption spectra is more accurate and easier than the Kramers-Kronig analysis and can be applied to more complicated geometry of the spectrum. The Kramers-Kronig analysis is used especially for thick surface films or for bulk materials.

The simultaneous fitting of several types of information related to the surface film leads to obtaining the correct values for n and k optical constants.

Highlighting the shift bands in the absorption spectrum is important for the understanding of different behavior of the polymer thin film as compared to the bulk polymer.

References

- [1] V.M. Zolotarev, B.Z. Volchek and E.N. Vlasova, *Optical constants of industrial polymers in the IR region*, Optics and Spectroscopy **101**(5), 716-723 (2006).
- [2] K. Nishikida, E. Nishio and W.R.Hannah, *Features and Operation Techniques of the Infrared Accessories*, in Selected Applications of Modern FT-IR Techniques, edited by Kodansha Ltd. Tokyo, pp. 51-53, (1995).
- [3] A.B.Kuzmenko, *Kramers-Kronig constrained variational analysis of Optical Spectra*, Review of Scientific Instruments **76**(8),083108.1-083108.9 (2005).
- [4] K. Yamamoto, *Optical theory applied to infrared spectroscopy*, Vibrational Spectroscopy, **8**, 1-36, (1994).
- [5] A.B. Kuzmenko, *Guide to Reffit: software to fit optical spectra* (2004) <<http://optics.unige.ch/alexey/reffit.html>>
- [6] S. Bădilescu, M. Giurginca, M. Toader and V. Tălpuș, *Spectroscopia în infraroșu a polimerilor și auxiliarelor*, București: Ed. Tehnică, pp. 141-143, (1982).
- [7] S.N. Kasarova, N.G. Sultanova, C.D. Ivanov, I.D. Nikolov, *Analysys of the dispersion of optical plastic materials*, Optical Materials **29**, 1481-1490 (2007).
- [8] W.R. Folks, J. Ginn, D. Shelton, J. Tharp J. and G. Boreman, *Spectroscopic ellipsometry of materials for infrared micro-device fabrication*, Phys.Stat.Sol. (c) **5**, No. 5, 1113-1116 (2008).
- [9] D. L. Allara, A. Baca and C.A. Pryde, *Distorsions of band shapes in external reflection infrared spectra of thin polymer films on metal substrates*, Macromolecules, **11**(6), 1215-1220 (1978).

Address:

- Conf. Dr. Simion Jitian, „ Politehnica” University Timișoara, Faculty of Engineering Hunedoara, Str. Revoluției, nr. 5, 331115, Hunedoara, jitian_s@fih.upt.ro