1. Simion JITIAN

THE USE OF IR-RA SPECTROSCOPY TO STUDY THE THERMAL DEGRADATION OF POLYVINYL ACETATE FILMS

1. University Politehnica Timisoara, faculty of Engineering Hunedoara, ROMANIA

ABSTRACT: To determine the optical constants of polymer films can be used both external specular reflection spectra and internal reflection spectra. The transmittance values measured in IR reflection-absorption (RA) spectra can be used to determine the optical constants of dielectric films laid on solid substrates. To obtain the optical constants of polymers 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. Using dispersion analysis offers the advantage of processing a large volume of data. The IR spectra of PVAc film deposited on steel recorded after its heat treatment, shows the appearance of a thermal degradation process of polymer.
KEYWORDS: Reflection-absorption, optical constants, IR spectra, dispersion analysis

INTRODUCTION

The study of reflection spectra of surface films deposited on solid media allow to determine the thickness and optical constants of these: the refractive index **n** and absorption index **k**.

The reflection of radiation on solid surfaces or transmission is expressed by its complex reflection $\tilde{r} = |\tilde{r}| \exp(i\vartheta)$ and transmission $\tilde{t} = |\tilde{t}| \exp(i\vartheta)$ coefficients. They depend on the complex refractive index of the film $\tilde{n} = n - ik$ and the angle of incidence φ_0. The reflectance, denoted R, is the ratio of reflected radiation intensity I_r and incident radiation intensity I_0, and is the square of the complex reflection coefficient: $R = r^2 = |\tilde{r}|^2$. The transmittance, denoted T, is the ratio of transmitted radiation intensity I_t and incident radiation intensity I_0 and is the square of the complex transmission coefficient $T = t^2 = |\tilde{t}|^2$.

To determine the optical constants of polymer films can be used both external specular reflection spectra and internal reflection spectra.
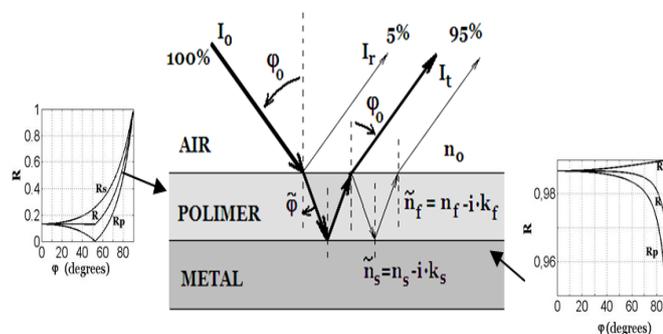

Figure 1. Specular reflection of radiation on thin films deposited on metals

For the specular reflection on thin polymer films (with thicknesses less than $2\mu m$) deposited on metals, as in Figure 1, the reflected radiation contains two components: one reflected by air-film interface (I_r intensity) and one reflected by film-metal interface (I_t intensity), after having twice crossed the polymer film.

The reflectance due to reflection at the air-film interface has values of about 5% because the values of refractive indices of polymers in the infrared region are less than 1.5. Meanwhile the reflectance at the polymer-metal interface has values over 99%. Thus, the radiation intensity reflected at the polymer-metal interface and twice crossing the polymer film is about 95% of incident radiation intensity, and almost 20 times greater than the beam directly reflected at the air-polymer interface.

Therefore, this spectrum is a reflection-absorption (or transflectance) spectrum, and is similar in terms of quality of transmission spectrum of the polymer film. This spectrum can be processed to obtain the optical constants **n** and **k** corresponding to the complex refractive index $\tilde{n} = n - ik$ [7].

The two optical constants can be obtained either from the reflectance measurements at two angles of incidence or using the whole range of reflectance spectrum values at one angle of incidence [5]. In the second case, Kramers-Kronig analysis of the recorded spectrum is used [10,11].

The dispersion analysis is another way to obtain the optical constants of thin films deposited on metal surfaces. It is more flexible than Kramers-Kronig analysis and can be applied to more complicated geometry of the spectrum.

Dispersion analysis is based on building an appropriate model for dielectric function and calculating the optical properties corresponding to this model. The

best known is Drude-Lorentz model [6, 9, 12] which defines the electric permittivity:

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

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 frequency range under consideration). The parameters ν_{pj}, ν_{oj} 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 permittivity, we can calculate all optical quantities such as reflectance R and transmittance T. The spectrum of these theoretically calculated quantities is compared with those experimentally determined. The model parameters 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 fitting parameters process stops when the differences between theoretical and experimental spectra are minimal.

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

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

$$\chi^2 = \sum_j^N \left(\frac{T_j^{exp} - T_j^{model}(\nu_j, p_j....p_M)}{\sigma_j} \right)^2 = \chi^2(p_1,....p_M) \quad (2)$$

Fitting process stops when the stopping criterion is met [8].

EXPERIMENTAL

Thin films of polyvinyl acetate (PVAc) were obtained by spraying a polymer solution on the surface of a steel metal sample. Low concentration of polymer in the solvent allowed us to obtain thin films with thickness less than 2μm. After evaporation of the solvent the IR reflection-absorption spectra at 20° incidence angle was recorded.

The metal sample coated with polymer film was then heated to a temperature of 80° C for 30 minutes to complete removal of the solvent. After the sample heat treatment we recorded IR reflection-absorption spectrum again. The metal surface used as substrate for the polymer film was obtained by grinding and polishing.

The IR reflection-absorption spectra were recorded using a specular reflectance device for UR-20 spectrograph.

The reflection-absorption spectra were processed using the program RefFIT [8] to obtain the optical constants of polymer film.

RESULTS AND DISCUSSION

The IR reflection-absorption spectra recorded at 20 degrees incidence angle are shown in Figure 2. The spectral range 500÷1800 cm^{-1} containing the absorption band at 1732 cm^{-1} corresponding to C = O stretching vibration is presented [3].

The reflectance R and hence the transmittance T values depend very least on the angle of incidence, as observed in Figure 1. Because of this, reflection-absorption spectrum at 20 degrees angle of incidence is very similar to the transmission spectrum for normal incidence.

Since the surface film thickness is less than 2μm, interference fringes in spectra recorded are not present [6]. For the same reason the spectrum recorded is one of reflection-absorption (transflectance).
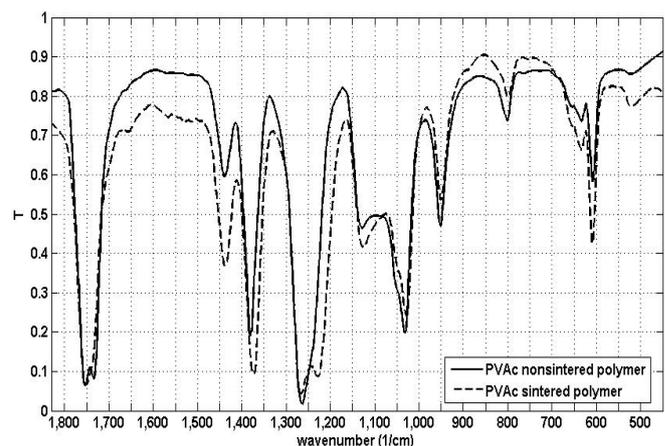

Figure 2. Reflection-absorption spectra at 20° incidence angle for a PVAc film deposited on polished steel

The IR spectra of PVAc film deposited on steel recorded after its heat treatment, shows the appearance of a thermal degradation process of polymer, which is its depolymerization.

The depolymerization process produces monomer units containing unsaturated C = C bonds. This is confirmed by increased of the absorption band at 1647 cm^{-1} characteristic for stretching frequency of C = C bond [2,3].

During thermal degradation is also possible to remove the acetic acid. This is highlighted by the change of vibration frequencies of C = O, C-O and C-C-O bonds. Thus, instead of stretching vibration frequencies of the C=O bonds at 1724 cm^{-1} and 1739 cm^{-1} there is a single band at 1752 cm^{-1}.

Instead of the absorption band at 1241 cm^{-1}, corresponding to vibration frequency of C-O bond appear two absorption bands at 1234 cm^{-1} and 1266 cm^{-1}. They correspond to C-O bonds in the acetate group linked to the macromolecular chain or partially released. Also, there is a decrease in the intensity of the absorption band at 1124 cm^{-1} corresponding to the vibrations of C-C-O bonds [3].

The spectra obtained can be processed to obtain the optical constants **n** (refractive index) and **k** (absorption index). We used 1381 points and 55 parameters in the fitting process.

To improve the accuracy of the dielectric function we used simultaneously the fitting process of reflection-absorption spectra recorded at a 20 degrees incidence angle and the refractive index of PVAc value $n_f = 1.4665$ [1].

The refractive index spectrum obtained by dispersion analysis of reflection-absorption spectrum for PVAc deposited on steel is shown in Figure 3.
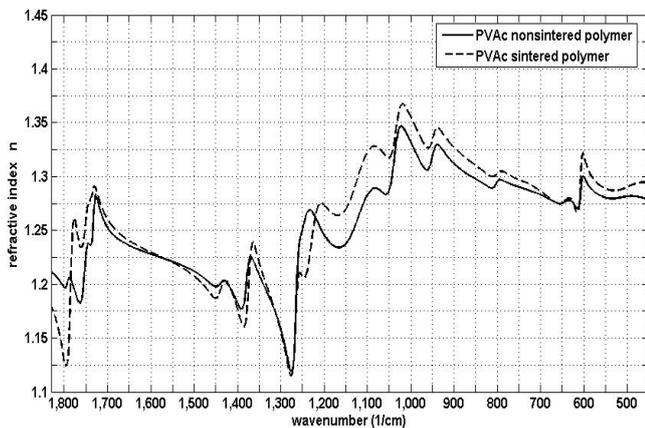

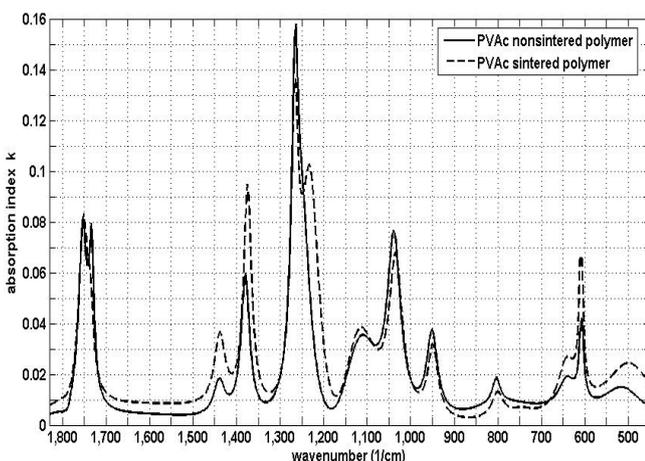Figure 3. Refractive index spectra for PVAc deposited on steel obtained by dispersion analysis

Figure 4. Absorption index spectra for PVAc deposited on steel obtained by dispersion analysis

The absorption index (extinction coefficient) **k** has a spectrum very similar to the absorption spectrum. The absorption coefficient spectrum of PVAc film deposited on steel is shown in Figure 4. The values of the absorption coefficient are low. The polymer can be considered to be almost transparent in infrared. In this spectrum, the absorption bands do not show deviations from the positions of the absorption bands in reflection-absorption spectrum.

Main frequencies of absorption bands of PVAc spectrum obtained by dispersion analysis of the reflection-absorption spectrum were presented in Table 1 and compared with those given in the literature [3]. 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. 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.

Table 1. The main spectral bands obtained by the dispersion analysis of the reflection-absorption spectrum of PVAc film in comparison with the literature [3]

Assignment	Transmission spectrum literature[3]		Reflection-absorption spectrum experimental			
			before treatment		after treatment	
	Intensity	ν_o	ν_o	k	ν_o	k
	-	cm^{-1}	cm^{-1}	-	cm^{-1}	-
ν(C=O)	very intense	1739	1753	0.0810	1752	0.0831
ν(C=O)	very intense	1724	1734	0.0796		
δ(CH$_2$) δ_a(CH$_3$)	intense	1433	1439	0.0186	1439	0.0368
δ_s(CH$_3$)	very intense	1374	1380	0.0598	1375	0.0949
ν(C-O)	very intense	1241	1264	0.1580	1266	0.1362
	very intense				1234	0.1027
νC-C-O	intense	1124	1129	0.0356	1114	0.0387
	intense	1047	1039	0.0766	1036	0.0682
ρ(CH$_3$)	intense	927	952	0.0378	950	0.0321
ν(CO-CH$_3$)	medium	796	802	0.0188	800	0.0134

CONCLUSIONS

The IR reflectance spectra for thin films (with thickness less than 2µm) are reflection-absorption spectra. The recorded size is the transmittance. Appearance of the reflection-absorption spectra is very similar in terms of quality to the transmission spectrum of the polymer.

The IR spectra of PVAc film deposited on steel recorded after its heat treatment, shows the appearance of a thermal degradation process of polymer, which is its depolymerization.

The dispersion analysis of reflection-absorption spectra is more accurate and easier than Kramers-Kronig analysis. The Kramers-Kronig analysis is used especially for thick surface films or for bulk materials.

Simultaneously fitting for several types of information about the film surface leads to accurate values of optical constants **n** and **k**.

REFERENCES

[1.] *** *TexLoc Refractive Index of Polymers*, www.texloc.com/closet/cl_refractiveindex.html ;

[2.] *Baker A.J. and Cairns T. Spectroscopy in Education, vol. 2, SpectroscopicTechniques in Organic Chemistry, Heyden & Son Ltd., London, 1967*

[3.] *Bădilescu S., Giurginca M., Toader M. and Tălpuş V., Spectroscopia în infraroşu a polimerilor şi auxiliarilor, Ed. Tehnică, Bucureşti, 1982;*

[4.] *Jitian S., Le traitement des spectres de reflection des couches dielectriques mince en vu de determiner leur epaisseur, Bul. Şt. Univ. Politehnica Timişoara, **39**(53)-1,2, 1994, p.107*

[5.] *[5] Jitian S. and Bratu I., The Use of Reflectance Infrared Spectroscopy for the Observation of the Polymeric Films on Metals, Studia Univ. Babeş-Bolyai, Physica, XXXI(2), p.30, 1986;*

[6.] *[6] Kiyoshi Yamamoto, Optical Theory Applied to Thin Films, Ph. Thesis, Case Western Reserve University, 1994;*

[7.] *[7] Koichi Nishikida, Etsuo Nishio and Robert W. Hannah, Selected Applications of Modern FT-IR Techniques, Kodansha Ltd, Tokyo, 1995;*

[8.] *[8]Kuzmenko A.B., Guide to Reffit: software to fit optical spectra, 2004, available online at: http://optics.unige.ch/alexey/reffit.html;*

[9.] *[9] Kuzmenko A.B., Kramers-Kronig constrained variational analysis of optical spectra, Review of Scientific Instruments, **76**(8), p. 083108.1-083108.9, 2005;*

[10.] *[10] Nilsson P.-O., Determination of optical constants from intensity measurements at normal incidence, Applied Optics, **7**(3), pp. 435-442, 1968;*

[11.] *[11] Palmer K.F. and Williams M.Z., Determination of the optical constants of a thin film from transmittance measurements of a single film thickness, Applied Optics, 24(12), p.1788, 1985;*

[12.] *Vettergren V.I., Smirnova N.S. and Chmel A.E., Classical dispersion analysis in determining optical constants from perturbed internal-reflection spectra, Zhurnal Prikladnoi Spektroskopii, **22** (2), p. 352, 1975*