Macromol. Symp. **2004**, *205*, 95—104

A Spectroscopic Ellipsometry Study of PET Membranes from IR to Vis-FUV

A. Laskarakis, M. Gioti, E. Pavlopoulou, N. Poulakis, S. Logothetidis*

Aristotle University of Thessaloniki, Department of Physics, GR-54124 Thessaloniki, Greece
E-mail: alask@physics.auth.gr

Summary: A detailed study of Spectroscopic Ellipsometry (SE) spectra of uniaxially stressed, 12μm thick poly(ethylene terephthalate) (PET) membranes were realized in both IR (900-3500 cm^{-1}) and Vis-FUV (1.5 to 6.5 eV) spectral regions and in various orientation angles ϕ between the plane of incidence and the machine direction (MD) of the PET membranes. In the IR spectra, the three main modes of the ester group at ~1126, 1256 and 1721 cm^{-1} are observed. The first two of these peaks show identical polarization dependence, with preferential orientation $\phi \approx 0°$ (i.e. the plane of reflection parallel to the MD), while the peak at ~1721 cm^{-1} is excited in the perpendicular direction, $\phi \approx 90°$. In the Vis-FUV SE spectra, the dependence of the characteristic electronic absorption bands on the orientation angle ϕ is studied. Besides the well known benzene band centered at ~5 eV, a doublet of less intense peaks appear just above the absorption edge between 4.1 and 4.3 eV with the most striking characteristic that they show polarization selection rules opposing to that of the benzene band. The above characteristics of the electronic Vis-FUV spectra of PET are discussed in a manner comparative to the corresponding IR spectra. The discussion becomes in the context of determining the molecular orientation of PET using a non-destructive technique such as SE.

Keywords: FTIR; membranes; optical properties; PET; spectroscopic ellipsometry

Introduction

During the past decades, polymer research exhibited a significantly increasing interest due to the large number of practical applications for polymeric membranes. The study of most of the interesting polymers is a complicated and a rather difficult procedure due to their optical anisotropy, which is the result of their molecular orientation and the fabrication process. Measurements of anisotropy are mostly performed at one wavelength by means of refractometry or prism coupling techniques.[1-3] However, the detailed characterization of the

DOI: 10.1002/masy.200450109

principal refractive indices in a wide spectral range from the infrared (IR) to the visible - far ultraviolet (Vis-FUV) spectral regions, is of great importance for many optical and opto-electronic applications.

Poly(ethylene terephthalate) (PET) has a great potential and it has been used in a wide range of industrial fields such as in the fabrication of high performance polarization optics due to its high anisotropy and to its relatively wide transparent spectral window,[4] and also in the field of plastic bottles, synthetic fibers, etc.[5] PET also demonstrates a combination of very important properties for packaging applications such as easy processing, good mechanical properties and reasonably high resistance to oxygen and carbon dioxide penetration (barrier properties).[6,7] Uniaxial or biaxial mechanical stretching is usually applied for the elongation of the polymeric membranes and their thickness reduction causing a preferable orientation of the macromolecules close to the surface and an ordered overlayer is formed which will be referred as “crystalline layer”.

In this work, the optical and electronic properties of PET are studied with the use of Spectroscopic Ellipsometry (SE). The accuracy and consistency of the results are assured by the comparative study of vibrational and electronic properties of PET in different spectral regions from IR to FUV. Until now, vacuum UV SE is open for scientific studies as all polymers exhibit multiple resonant-type absorptions in the UV most of which have been little studied. The most recent literature for this issue is based on SE studies in a narrow energy range at Vis-UV region where polymers are more or less transparent, thus little and ambiguous information can be derived about their optical and electronic properties.[8]

Experimental

The examined PET membranes were industrially supplied samples of a thickness ~12 μm treated with mechanical stretching that is usually applied in industrial scale. This procedure resulted to the formation of a crystalline-like layer on top of the membrane of unknown thickness. The Vis-FUV spectra measurements were performed by using a Phase Modulated Ellipsometer (PME) over the energy range 1.5-6.5 eV. This unit is consisted of two photomultiplier detectors; one for the Vis-UV range (1.5-4.0 eV) and one for the UV-FUV range (4.0-6.5 eV).

The IR measurements were performed in the range of 900-3000 cm^{-1}, using a Fourier transform IR Phase Modulated Ellipsometer adapted to the ultra high vacuum deposition chamber using BaF_2 windows. The IR beam is produced by a commercial IR spectrometer (BOMEM-MB100) which includes a thermal source of SiC bars and a Michelson interferometer and is focused on the sample through an optical system of reflectors and lenses. A grid analyzer and a photo-elastic modulator, which modulates the IR beam polarization with a frequency of 37 kHz, define the polarization of the incident beam. After its reflection on the sample, the polarization of the IR beam is detected by a grid analyzer and then is focused on the detection head through a suitable optical system. The spectra in both IR (900-3000 cm^{-1}) and Vis-FUV (1.5 to 6.5 eV) spectral regions have been acquired using various orientation angles φ between the plane of incidence and the machine direction (MD) of the PET films. The sequential spectra were recorded by rotating the sample with a step of 60°, to φ angles from 0° to 180°. Also, the monomer of PET which is the basic unit that constitutes the PET macromolecules is presented in Fig. 1b.

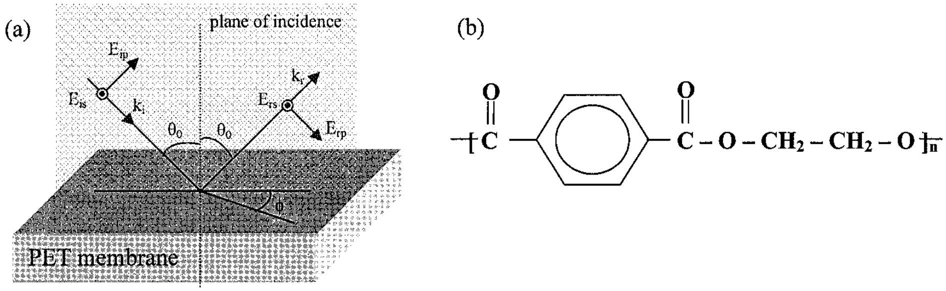

Figure 1. (a) Definition of the orientation angles, (b) the monomer of PET

Results and Discussion

The measured quantity by SE is the *pseudodielectric function* $<\varepsilon(\omega)>$ in case for a thin transparent film grown on a bulk substrate or generally for transparent materials (such as PET membrane). $<\varepsilon(\omega)>$ provides information both on dielectric response and thickness of the films as it can be seen in the typical Vis-FUV spectra of PET membrane illustrated in Fig. 2. The interference fringes observed in the energy range 1.5–4.0 eV are the result of the multiple reflections of the beam at the interfaces of the measured sample and reveal the optical transparency of PET in that energy region. Two kinds of interference fringes with different periodicities are observed. The first kind, clearly evident from 1.5 to 2.5 eV is characteristic of the amorphous membrane while the second kind with longer periodicity from 2.5 to 4 eV is due to a thin crystalline-like overlayer.[9]

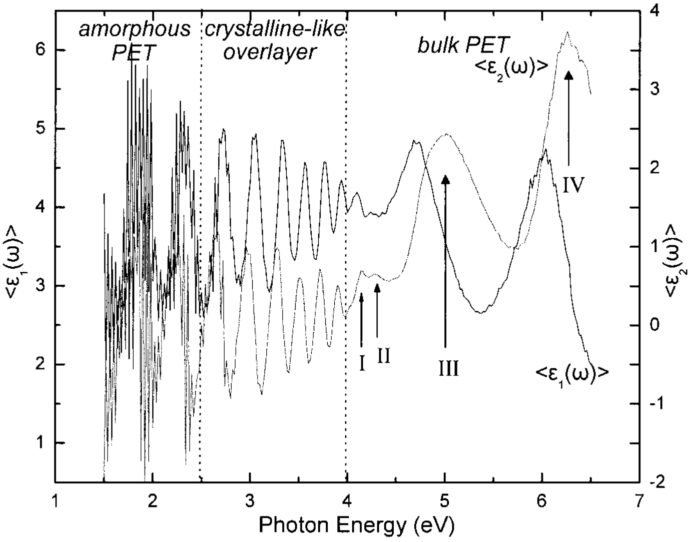

Figure 2. The <ε(ω)> spectra of the PET membrane in the Vis-FUV spectral range as measured by Vis-FUV SE.

In the Vis-FUV spectral region the absorption edge lies at about 4 eV where the Vis-FUV spectrum is dominated by four characteristic features. A doublet of low intensity peaks, just above the absorption edge at around 4.15 (peak I) and 4.3 eV (peak II) and two other stronger bands centered at around 5 (peak III) and 6.2 eV (peak IV) are observed. The energy location of these electronic transitions is characteristic for the PET, however, a strong dependence is observed between their strength and the orientation angle φ, which is very pronounced by Fig. 3 where the $<\varepsilon_2(\omega)>$ spectra for different values of φ are plotted.

The differences among the imaginary part of the pseudodielectric function of various angles φ come from the optical anisotropy of PET, as it can be seen in Fig.3. Peaks I and III are strongly polarization dependent whereas peaks II and IV are almost independent with the change of the orientation angle φ.

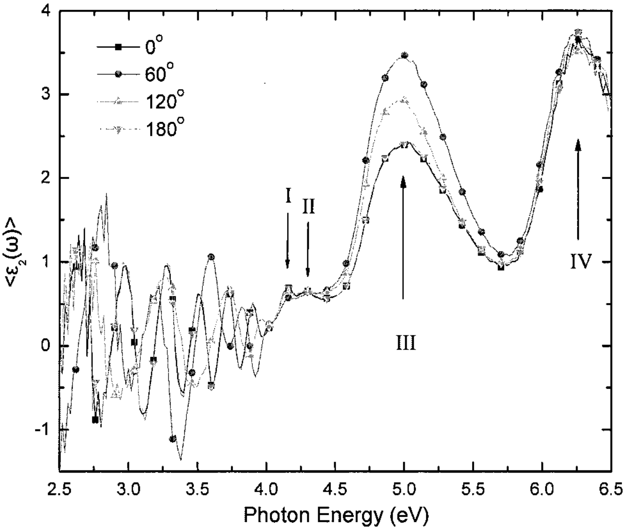

Figure 3. The imaginary part of $<\varepsilon(\omega)>$ spectra of the PET membrane in the Vis-FUV spectral range in various values of angles φ between the MD and the plane of incidence.

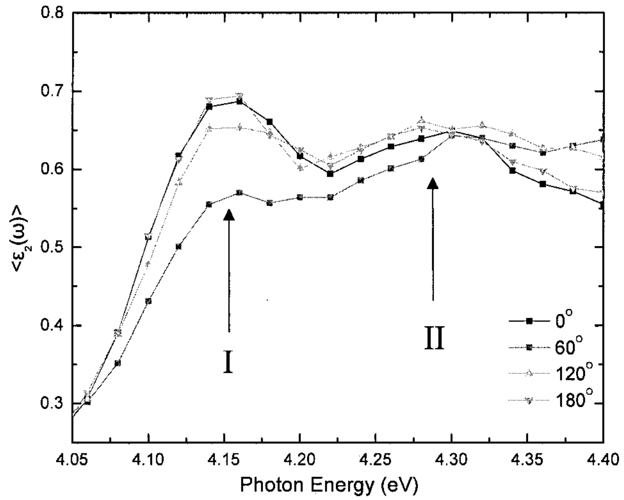

Figure 4. A more detailed view of the imaginary part of <ε(ω)> spectra of the PET membrane that shows the two less intense absorption peaks and their dependence with the orientation angle φ.

Both peaks I and II that are observed at ~4.1 and ~4.3 eV can be attributed to the electronic transition of the carbonyl O lone pair (non-bonding) electron from the n state to the π* unoccupied valence state orbital of C=O bond (transition: $n_O \rightarrow \pi^*$).[10] This is a relatively weak transition due to the fact that this is symmetry forbidden.[10] The appearance of two peaks corresponding to this transition can be a direct result of the macromolecular distribution of the PET monomers in the membrane, since the position of the $n_O \rightarrow \pi^*$ transition is quite dependent on the immediate environment of the carbonyl group. More specifically, peak I can be attributed to the carbonyl O lone pair electronic transition $n_O \rightarrow \pi^*$ of the oriented regions of the crystalline like overlayer. This is justified by both its polarization dependence and its lower broadening characteristics. Moreover, the electronic excitation of the carbonyl O lone pair electrons at the unoriented regions of the membrane gives rise to peak II. The peak's appearance in a higher energy can be explained in terms of the stabilization of the lone pair by hydrogen bonding due to the immediate environment of the C=O group at the unoriented regions of the membrane. The correlation of the peak II with this transition is also supported by its broad structure and the weaker dependence with polarization.

The peak III can be attributed to the spin-allowed, orbitally-forbidden $A_{1g} \rightarrow B_{2u}$ electronic transitions in molecular orbitals of benzene rings.[10] The high broadening of peak III can be the result of the break of the symmetry due to the substitution of the 1,4 ring carbon atoms.[10] Finally, the peaks IV might be attributed to the $A_{1g} \rightarrow B_{1u}$ valence electronic transitions respectively of the parasubstituted benzene ring of the PET molecule with polarization selection rules on the plane of the ring, however, further investigation is needed for the accurate interpretation of the SE data and results and the assignment of the observed features. Fig. 5 shows a typical IR SE spectrum obtained from PET membrane. Due to the increased sensitivity of the FTIRSE technique the IR spectrum includes all the strong bands of PET which are difficult to distinguish with other techniques. In the spectral range from 900 to 1800 cm^{-1} the contribution of vibrational modes corresponding to the IR active chemical bonds of PET is appeared. Above 1800 cm^{-1} the spectrum is dominated by interference fringes due to the multiple reflections of IR beam at the interfaces of the measured PET membrane.

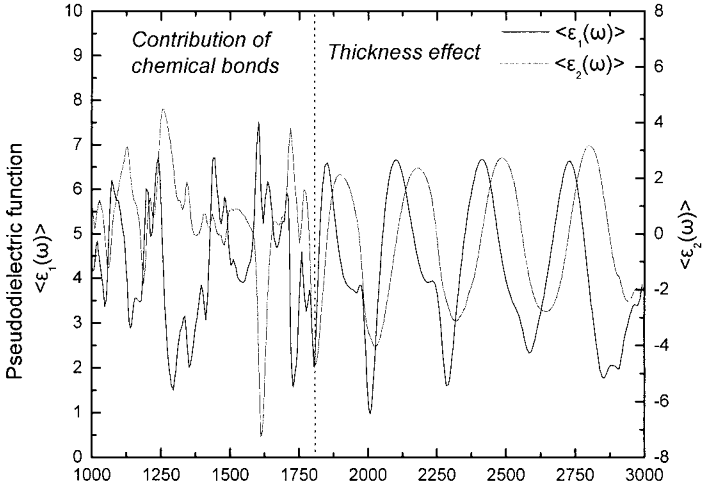

Figure 5. The real ($<\varepsilon_1(\omega)>$) and imaginary ($<\varepsilon_2(\omega)>$) parts of the pseudodielectric function of PET membrane in the IR spectral region as measured by IR SE.

Although the energy of the vibrational modes is characteristic for the PET, the strength of each vibrational mode is strongly affected by the membrane's orientation with respect to the plane of incidence. This is shown in Fig. 6, where the imaginary part of the <ε(ω)> spectra measured for different orientation of the membrane is illustrated. The observed differences in the strength of the vibration modes are the result of the optical anisotropy of PET.

Among the more intense bands, we observe in the IR SE spectra the characteristic bands corresponding to the vibration modes of the *trans* C-O stretch (~976 cm^{-1}), the ester C-C, C-O stretch (~1024 cm^{-1}), the ethylene glycol CH_2 wagging mode (~1342 cm^{-1}), the in-plane deformation of the C-H bond of the parasubstituted benzene rings (~1024 and ~1408 cm^{-1}). Also, we observe the characteristic bands corresponding to the stretching modes of the ethylene glycol and ester groups at ~1126 and ~1256 cm^{-1} the aromatic and ethylene glycol CH_2 stretching mode (1658 cm^{-1}) and the carbonyl (C=O) stretching mode at ~1721 cm^{-1}. [11,12]

From Fig. 6 it is obvious that the vibration modes corresponding to the stretching modes of *trans* C-O bonds show opposite polarization dependence to the peak at 1721 cm^{-1} (C=O stretching mode). Moreover, the characteristic bands corresponding to the vibration modes of the aromatic rings and esters at 1126 and 1256 cm^{-1} show identical polarization dependence and opposite to the carbonyl band. Also, the above characteristic features contribute more to the IR spectra of the PET membrane measured at orientation angle $\varphi \approx 60°$ while the peak of the carbonyl C=O stretching mode is strongly excited in the perpendicular direction, $\varphi \approx 120°$.

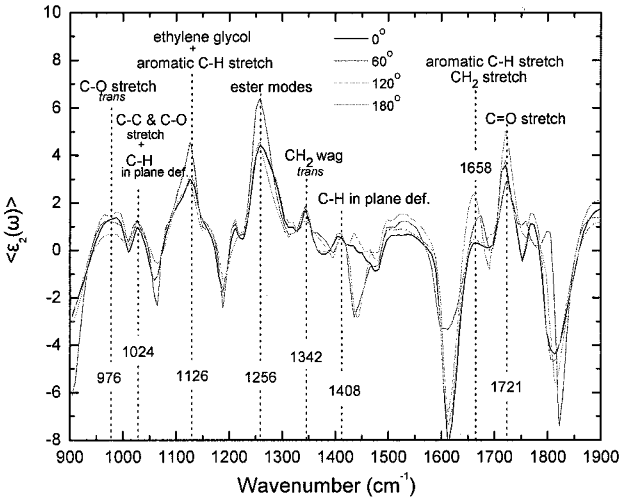

Figure 6. The imaginary part <$\varepsilon_2(\omega)$> of PET membrane in the IR spectral region in various orientations with respect to the plane of incidence.

The above observations are in accordance with Vis-FUV spectra measurements of the PET membrane. In particular, peak III and peaks I & II exhibit opposite polarization dependence. Since peak III can be attributed to the electronic transitions of the benzene rings and the peaks I and II to the carbonyl O electron lone pair, therefore we are drawn to the conclusion that the studied PET membrane exhibits a preferential orientation of the PET macromolecules to an angle of ~60° with respect to the MD of the membrane.

Conclusions

PET membranes were studied by means of SE from IR (900–3000 cm^{-1}) to Vis-FUV (1.5–6.5 eV) spectral range. The optical anisotropy of PET membrane was evident by the <$\varepsilon_2(\omega)$> spectra recorded in different orientations of the membrane MD with respect to the plane of incidence in both spectral regions. The Vis-FUV <$\varepsilon_2(\omega)$> spectra revealed four characteristic peaks at 4.1, 4.3, 4.9 and 6.1 eV attributed to electronic transitions that take place at specific molecular orbitals of the PET monomer, in view of their symmetry. From the IR SE spectra we studied the vibrational modes of the IR active bonds of PET and in combination with the Vis-FUV spectra we estimated the preferential orientation of the PET macromolecules of the crystalline-like overlayer. The vibration modes of the ethylene glycol, esters and the C-O bonds showed opposite polarization dependence to the characteristic vibration mode of the carbonyl C=O group at 1721 cm^{-1}. The above led to the conclusion that PET macromolecules must have a preferential orientation at ~60° with respect to the MD. The above methodology proves the potentiality of the SE in both IR and Vis-FUV spectral regions which in combination with its *in situ* and real time capabilities can provide valuable information about rapid polymer changes during processing.

Acknowledgements

This work was supported by the EU GROWTH Project – TransMach (Contract No: G1RD-CT-2000-000334) and partly by the Greek General Secretariat for Research and Technology under the project PENED-2001 ED 256.

[1] J. Jager, J.A. Juin, C.J.M. van der Heuvel, R.A. Huijts, *J. Appl. Polym. Sci.* **1995**, *57*, 1429.
[2] V. Lorenzo, J.M. Perena, *J. Appl. Polym. Sci.* **1994**, *39*, 1467.
[3] S.S. Hardaker, S. Moghazy, C.Y. Cha, R.J. Samuels, *J. Polym. Sci. Part B (Polym. Phys.)* **1993**, *31 (13)*, 1951.
[4] Y. Dirix, H. Jagt, R. Hikmet, C. Bastiaansen, *J. Appl. Phys.* **1998**, *83 (6)*, 2927.
[5] Y. Wang, S. Lehmann, *Applied Spectroscopy* **1999**, *53 (8)*, 914.
[6] M. Yanaka, B.M. Henry, A.P. Roberts, C.R.M. Grovenor, G.A.D. Briggs, A.P. Sutton, T. Miyamoto, Y. Tsukahara, N. Takeda, R.J. Chater, *Thin Solid Films* **2001**, *397*, 176.
[7] A.E. Tonelli, *Polymer* **2002**, *43*, 637.
[8] K. Forcht, A. Gombert, R. Joerger, M. Kohl, *Thin Solid Films* **1998**, *313–314*, 808.
[9] S. Logothetidis, M. Gioti, C.Gravalidis, *Synthetic Metals* **2003,** *1-6*, 10358.
[10] D. C. Harris, M. D. Bertolucci, "*Symmetry and Spectroscopy*", Dover Publications New York 1978, pp. 373-379.
[11] K.C. Cole, A. Ajji, E. Pellerin, *Fourier Transform Spectroscopy, 11th International Conference*, edited by J.A.de Haseth 1998.
[12] C.E. Miller, B.E. Eichinger, *Applied Spectroscopy*, **1990**, *44 (3)*, 496.