Optical and Morphological Properties of P3HT and P3HT: PCBM Thin Films Used in Photovoltaic Applications

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Abstract. This work is focused on the study of some physical properties of poly(3-hexylthiophene-2,5-diyl) (P3HT) and poly(e-hexylthiophene-2,5-diyl): Methanofullerene Phenyl-C61-Butyric-Acid-Methyl-Ester (PCBM) blend thin films. Knowing the polymer advantages, such as ease of processing, high thermal stability, strong interaction with light, its properties have captured the attention regarding the changes that can occur in a polymer:fullerene blend in term of them. Polymer and polymer:fullerene blend (1:0.1, 1:0.2, 1:0.4 and 1:0.8 ratios) were deposited by spin coating on glass and SnO$_2$:F (FTO) coated glass. The optical properties were emphasized using spectrophotometry (300 – 2200 nm wavelength range) and spectroscopic ellipsometry models, to obtain the refractive index, extinction coefficient and the transmission (found higher than 80%). According to X-ray diffraction analysis, as-obtained films are amorphous. Investigation of the surface morphology of thin-film samples using Atomic Force Microscopy revealed a crystallite-like surface morphology with crystallite size in the nanometer range.

1. Introduction
Organic solar cells exhibit a huge potential in solar energy harvesting, in particular due to their great versatility in the manufacturing methods and low cost of raw materials. Polymers have become materials of great interest for photovoltaic applications due to the peculiarities and advantages they offer. These are cheap and inexhaustible materials and they can be easily processed even at low temperatures [1].

Found in a wide range of colours, the peculiarities of their interaction with light make them promise for use in solar cells (polymer-based photovoltaic cells). Being flexible, polymers can be deposited on different substrates. They show optical and electric properties that can be improved by doping with different materials (in the present study, fullerene). Disadvantages of polymer materials also include high sensitivity to oxygen, water etc., but these can be limited by device encapsulation. The cost of polymer solar cells remains high due to the incipient state of the study in this field [2].

This paper considers some characteristics of polymer thin films of poly(3-hexylthiophene) (P3HT) and Methanofullerene Phenyl-C61-Butyric-Acid-Methyl-Ester (PCBM). The interest in using these
two organic materials is motivated by the fact that P3HT is a conductive $\pi$-conjugated polymer used in a bulk-heterojunction solar cell structure as $p$-type material active layer and PCBM is a fullerene used in solar cell active layer as a $n$-type material [3, 4].

2. Materials and methods

Highly regioregular (>98%) polymer, poly(3-hexylthiophene) (P3HT), purchased from Rieke Metals, and Methanofullerene Phenyl-C61-Butyric-Acid-Methyl-Ester (PCBM), purchased from Ses Research, were used in different weight ratio blends (1:0, 1:0.1, 1:0.2, 1:0.4 and 1:0.8), to obtain thin films deposited on glass and SnO$_2$:F (FTO) substrates by spin coating in normal atmosphere at room temperature.

The thicknesses of these samples (Table 1) were measured by profilometry, using a VEECO Dektak 6M Stylus Profilometer, and compared with the thickness values measured by spectroscopic ellipsometry technique, using a UVVISELTM ellipsometer from Horiba Jobin Yvon.

| Sample | Weight ratio (P3HT:PCBM) | Thickness by profilometry (nm) | Thickness by ellipsometry (nm) |
|--------|--------------------------|-------------------------------|-------------------------------|
| Ps0    | 1:0                      | $\approx$ 120                | 93 ± 3                        |
| Ps0.1  | 1:0.1                    | $\approx$ 180                | 211 ± 1                       |
| Ps0.2  | 1:0.2                    | $\approx$ 150                | 186 ± 3                       |
| Ps0.4  | 1:0.4                    | $\approx$ 160                | 270 ± 5                       |
| Ps0.8  | 1:0.8                    | -                             | 299 ± 1                       |

The optical properties were emphasized by means of two methods of characterization, spectrophotometry and spectroscopic ellipsometry. The transmittance spectra of polymer and polymer: fullerene blend thin films were recorded in the spectral range from 300 to 2200 nm, by a double beam LAMBDA 950 UV/Vis/NIR spectrophotometer. Complementary, in the same wavelength range and at room temperature, a UVVISELTM ellipsometer with a 75 W high discharge Xenon lamp was used [5-7]. The structural and morphological properties were investigated using a Brucker D8 Advance X-ray diffractometer (nickel-filtered CuK$_{\alpha1}$ radiation, $\lambda$=1.5406 Å) and a contact mode atomic force microscope (AFM), respectively [8–10].

3. Results and discussions

Graph 1 (left) represents the transmittance values for P3HT and P3HT:PCBM blend thin films. From this graph, it appears that the transmittance is influenced by the amount of fullerene, as follows: in the infrared spectral range, increasing the quantity of fullerene, the transmittance decreases visibly; in the visible spectral range, instead, there is a reversal so that the amount of fullerene improves the transmittance, which is between 20 and 60%.

Another specific characteristic determined by the processing of the experimental data recorded by spectrophotometry is the calculation of the optical band gap using Tauc relation. From the dependence of the absorption coefficient on the incident photon energy (Graph 1 - right), the optical band gap for P3HT was found equal to 1.90 eV.
Figure 1. Transmittance spectra of P3HT and P3HT:PCBM thin films (left) and the optical band gap determination of P3HT polymer (right).

Ellipsometry is an optical characterization technique, indirect and nondestructive. The experimental data obtained are compared with those generated by the ellipsometric model based on new amorphous dispersion formula (1):

\[
n(\omega) = n_\infty + \frac{B(\omega-\omega_j)+C}{(\omega-\omega_j)^2+\Gamma_j^2}, \quad k(\omega) = \begin{cases} 
\frac{f_j(\omega-\omega_j)}{(\omega-\omega_j)^2+\Gamma_j^2}, & \text{for } \omega > \omega_g \\
0, & \text{for } \omega < \omega_g 
\end{cases} (1)
\]

where:

\[
\begin{align*}
B_j &= \frac{f_j}{\Gamma_j} \cdot \Gamma_j^2 - (\omega_j - \omega_g)^2 \\
C_j &= 2 \cdot f_j \cdot \Gamma_j \cdot (\omega_j - \omega_g)
\end{align*}
\]

In expression (1) and (2), \( n \) denotes the refractive index, \( k \) represents the extinction coefficient, \( f_j \) is the oscillator strength (amplitude of the extinction coefficient) (0 < \( f_j \) < 1), \( \Gamma_j \) is broadening factor of absorption peak (0.2 < \( \Gamma_j \) < 8), \( \omega_j \) represents the energy for which the extinction coefficient is maximum (1.5 < \( \omega_j \) < 10), while \( \omega_g \) is the energy at which the extinction coefficient is minimum (\( \omega_g < \omega_j \)). All these parameters are expressed in electron-Volts (eV).

Relation (3) describes the fundamental relation of ellipsometry which governs Graph 2, containing the reflection ellipsometric ratio (\( \rho \)), amplitude ratio, \( \Psi \), and phase difference, \( \Delta \), by which the refractive indices, extinction coefficients and dielectric constants corresponding to each sample will be extracted, depending on the fullerene amount:

\[
\rho = \frac{r_p}{r_s} = \tan \Psi e^{i\Delta}.
\] (3)

Here, \( r_p \) and \( r_s \) represent the reflection coefficients of light polarized parallel, respective perpendicularly to the plane of incidence.
Applying definitions of refractive index and coefficient of extinction, from the dispersion formula (1), we obtain Graph 3, representing the dependence of the refractive index, \( n \), on the wavelength.
(Graph 3 - left) and spectral dependence of the extinction coefficient, $k$, (Graph 3 - right), considering the dopant amount. Thus, in the visible range, both the refractive index and the extinction coefficient decrease with the increase in the fullerenes amount. In the graph of the extinction coefficient, the fingerprints of the two constituents (polymer and fullerene) is clearly visible, given the relationship between this coefficient and the absorption coefficient [7, 11].

Figure 3. Spectral dependences of the refractive index, $n$, (left) and the extinction coefficient, $k$, (right).

Starting from the definition (formula 4) of the complex refractive index, the dielectric constant, $\varepsilon$, can be determined (formula 5), in which $\varepsilon_r$ is the real part and $\varepsilon_i$ is the imaginary part of the it.

$$\tilde{n} = n - ik; \quad (4)$$

$$\tilde{\varepsilon} = (\tilde{n})^2 = \varepsilon_r - i\varepsilon_i. \quad (5)$$

Like the refractive index, the dielectric constant (Graph 4) depends on the amount of fullerene, decreasing together with the increasing fullerene concentration.

From the X-ray diffractograms, a predominantly amorphous nature was found, irrespective of the amount of fullerene, with a small intensity peak corresponding to the polymer, at $2\theta \approx 5$ degrees, and another peak located at $2\theta \approx 10$ degrees, corresponding to the fullerene.

Figure 4. Spectral dependence of the dielectric constant: the real part (left) and the imaginary part (right).
According to AFM analysis, there are not significant changes in polymer and polymer:fullerene blend morphologies. But regarding thin-film deposition on different substrates, glass and FTO, the influence of the FTO substrate on the thin film morphology was clearly manifested: measured roughness values range between 3 and 10 nm for deposits on the glass and between 25 and 30 nm for those on FTO (with a FTO roughness of about 34 nm).

4. Conclusions
In summary, polymer thin films deposited by spin coating at room temperature, with a thickness between 150 and 200 nm, were optically, morphologically and structurally characterized using different techniques. Depending on the P3HT:PCBM weight ratio, they exhibit peculiarities in the optical properties variation (decreasing the refractive index, extinction coefficient and dielectric constant, depending on the amount of fullerene). Considering the influence of both weight ratio and substrate nature, from the point of view of samples morphology, the roughness increases with the increase in the fullerene amount and it is influenced by the substrate roughness.

5. References
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