

Research Article

A Simple Optical Model for the Swelling Evaluation in Polymer Nanocomposites

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In the present study, we report on a simple optical method based on thin film interferometry for the swelling evaluation in polymer nanocomposite layers used for gas sensing applications. We show that white light interferometry can be profitably applied to characterize scattering materials such as polymer/carbon black nanocomposites. A properly adjusted experimental setup was implemented to monitor the swelling behavior of the sensitive films in real device operating conditions. In particular, the behavior of poly(2-hydroxyethyl methacrylate) (PHEMA) and of carbon black/PHEMA nanocomposite layers, used for volatile organic compounds (VOCs) detection, was investigated and measured under ethanol vapors exposure (max 1%). The method is very sensitive and the swelling in the range of only few nanometers can be measured. Interestingly, we have found that the nanocomposite undergoes a more pronounced swelling process with respect to pristine polymer. Ethanol diffusion coefficients in the nanocomposite were evaluated.

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1. Introduction

Polymer films and their nanocomposites embedded in polymer matrix are well known to be sensitive to different analytes and are extensively used in sensing application where their different transduction properties (such as electrical, mechanical, and thermal properties) are exploited. The target set by the research in this area is the device response optimization in terms of sensitivity, selectivity, and stability [1]. Polymer nanocomposite-based chemical sensors work on the basis of a change of their electrical properties when they come into contact with a specific substance. Due to the solvent absorption, the volume of the polymer matrix increases (swelling) and, at the same time, the volumetric fraction of carbon particles decreases [2–5]. Therefore, the change in film volume results in a modification of the conduction paths throughout the film that is measured as a change in the electrical resistance.

Swelling measurement is thus very important to study the sensing layer operating mechanism and to optimize the sensor device performances.

Device optimization needs a comparison between electrical response and film expansion under volatile organic compounds (VOCs) exposure.

Optical methods, such as white light interferometry, are commonly used in commercial measuring system [6] to estimate transparent film thickness on reflective substrate. These method have the advantage to be non-contacting techniques. However, when applied to swelling evaluation, any optical method generally fails in two respects: (i) the swelling changes the distance between the optical probe and the sample; (ii) nanocomposites generally behave as strongly scattering material. Therefore, during analyte absorption, it may become very difficult to ascertain if the observed variation in the reflectance is due to the swelling or to the effect of the sample scattering. A method based on

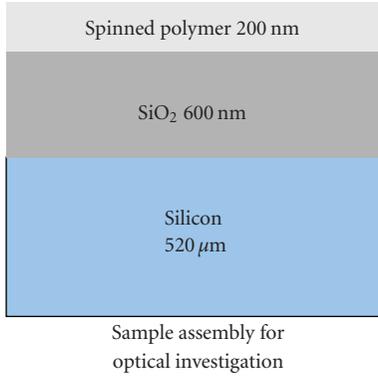


FIGURE 1: Section device scheme for optical investigation.

white light interferometry for the evaluation of the swelling of nonscattering materials, such as poly(2-hydroxyethyl methacrylate) (PHEMA), has been already proposed [3].

Here we show that white light interferometry can be profitably used for the swelling evaluation of scattering materials such as polymer/carbon black nanocomposites. Problems resulting from the change in the distance between the film and the optical probe have been overcome by a properly adjusted experimental setup as the relative change in film thickness during swelling is negligible with respect to the probe to sample distance.

Swelling of PHEMA/carbon black- (CB-) sensitive films in sensor devices operating in real conditions was evaluated.

2. Optical Model

Hereafter, the main assumptions and approximations of the proposed optical model are reported.

In Figure 1, a schematic picture of the polymer nanocomposite-based sensor investigated in this study is shown. The film thickness, together with the conductive filler content and the transducers geometry, determines the device impedance that must be considerably lower than the one of the substrate. From the optical point of view, the film thickness together with the carbon black content determines the optical absorbance and scattering and, in turn, affect the fringes contrast. As a consequence, the resulting tradeoff nanocomposite film thickness for our experimental setup ranges between 100 and 300 nm.

The system depicted in Figure 1 may be optically considered as composed by a nonabsorbing double layer onto an infinite thick substrate. In this frame, the SiO₂ layer has a double function: (i) electrical insulator; (ii) buffer layer to increase the optical path and thus the number of fringes in the interference spectra. In Table 1, the refractive indices and the extinction coefficients, in the visible range of PHEMA, SiO₂, CB, and ethanol are reported [7–9]. Bruggeman approximation [10] was used to evaluate refractive index for polymer composite.

Data show that the refractive indices of PHEMA and PHEMA/CB in the 400 nm–900 nm wavelength range differ by less than 1% and are very similar, in this range, to

TABLE 1: Refractive indices and extinction coefficients of the used materials; $\langle n \rangle$ is the weighted mean value for polymer nanocomposite.

Material	n	k	Weight (%)	Thickness (nm)	$\langle n \rangle$
SiO ₂	1.45	~0		600	
PHEMA	1.51	~0	98.5%	266	
CB	2	1	1.5%		
C ₂ H ₅ OH	1.33	~0	0.37%		
PHEMA/CB				866	1.520
PHEMA/CB/C ₂ H ₅ OH				866	1.524
SiO ₂ /PHEMA/CB/				866	1.488

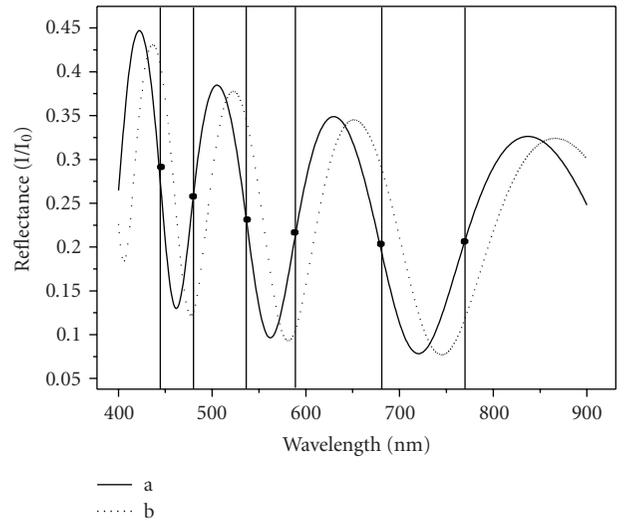


FIGURE 2: (a) reflectance spectrum of a 866 nm thick PHEMA layer; (b) fringe shift for a swelling of 30 nm. Black dots indicate inflection points.

the SiO₂ refractive index. Under such approximations, the double layer can be optically modeled as a single optical layer with an average refractive index, $\langle n \rangle$, that is the weighted mean between the SiO₂ and polymer layer refractive indices, according to the Bruggeman approximation [10].

Thus, the optical reflectance for the system depicted in Figure 1 is given, within a maximum 4% error, by

$$R = \frac{r_1^2 + r_2^2 + 2r_1r_2 \cos 2\theta}{1 + r_1^2r_2^2 + 2r_1r_2 \cos 2\theta}, \quad (1)$$

where, r_1 and r_2 are the reflectance between the first and second interface and between the second and the third interface given, respectively, by

$$r_1 = \frac{(n_0 - \langle n \rangle)}{(n_0 + \langle n \rangle)}, \quad r_2 = \frac{(\langle n \rangle - n_2)}{(\langle n \rangle + n_2)}, \quad (2)$$

and θ is the phase thickness of the coating

$$\theta = \frac{2\pi n_1 d_1}{\lambda}, \quad (3)$$

n_0 , $\langle n \rangle$ and n_2 are the air, the effective layer, and the substrate refractive indices, respectively. d_1 is the total thickness of the effective single layer.

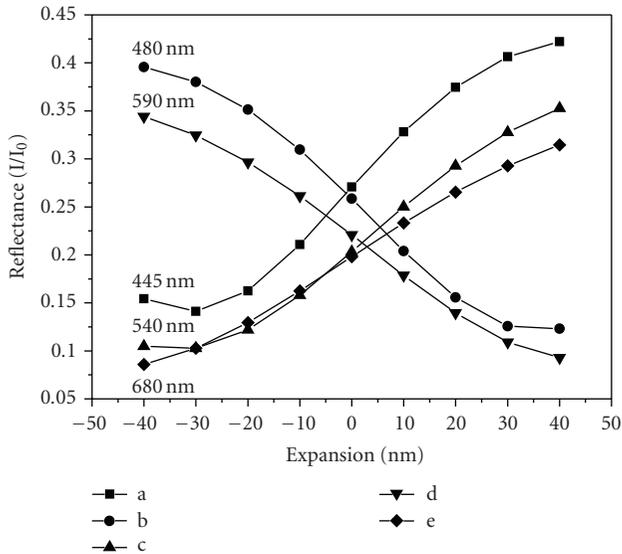


FIGURE 3: Simulated reflectance vs swelling for a 866 nm thick layer taken at the five inflection point wavelength: (a) negative inflection point (IP) at 445 nm; (b) positive IP at 480 nm; (c) negative IP at 540 nm; (d) positive IP at 590 nm

It is worth noting that for the PHEMA/CB (5%) composite (n) is the same as the layer with sole polymer within an error of less than 1%. The same is true for the nanocomposite upon absorption of up to 10000 ppm of ethanol, as shown in Table 1.

From the spectrum minima or maxima, both the layer thickness and the refractive index can be evaluated.

The model suggests that a variation in the single layer thickness (e.g., due to the swelling) will result in a modification of the optical reflectance spectra.

In Figure 2 the effect of 30 nm polymer swelling on the optical spectrum is shown. As expected, the film expansion produces a fringe shift. It can be noted that the curve slope near the inflection points quite rigidly translates. The resulting thickness variation may be particularly marked: at a fixed wavelength a less than 4% variation of the total thickness yield a reflectance variation larger than 50%.

This effect is more clearly visible in Figure 3 where the theoretical variation, at a fixed wavelength, of the reflectance intensity as a function of the layer expansion is reported. The model shows that if we fix the wavelength at an inflection point, a ± 15 nm thickness variation results in a $\pm 40\%$ linear reflectance change, so that extremely small swelling values can be evaluated.

3. Experimental

The PHEMA series of samples were prepared by dissolving the polymer (4 wt%) in hexafluor-2-propanol (HFIP), while the PHEMA/CB layers were obtained by dispersing carbon black Pearls 2000 (CABOT Corporation) (5.5 wt% with respect to polymer) in the PHEMA (1 wt%)/HFIP solution. The carbon black content is determined on a weight basis

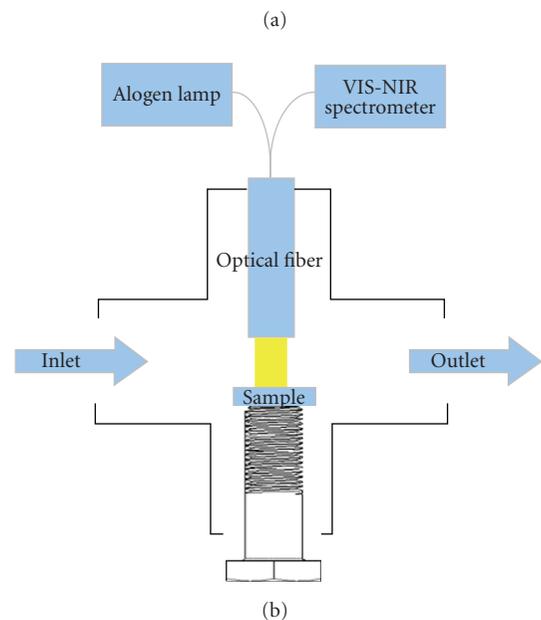
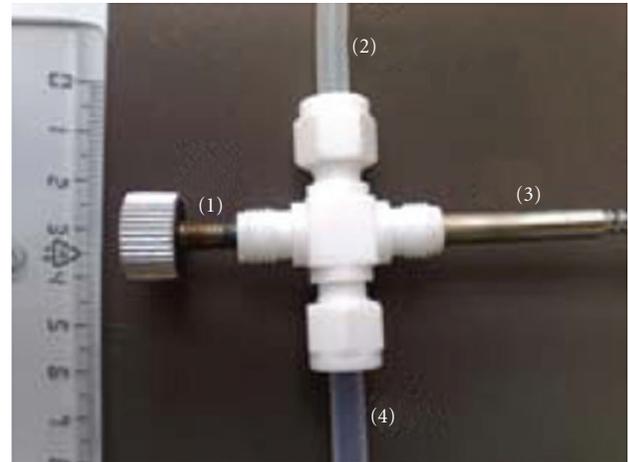


FIGURE 4: (a) photograph of the chamber for optical characterization in controlled environment: (1) sample holder, (2) gas inlet, (3) fiber optic holder, (4) gas outlet; (b) a scheme of the chamber for optical characterization.

of the components in the starting dispersion. Characterizations by means of Thermogravimetric Analysis (TGA) on PHEMA/CB nanocomposite film have shown that the weight ratio, polymer/filler, in the dispersion is preserved in the deposited film.

After sonication, the solutions were spin-coated on SiO_2 coated crystalline Si wafers. For this study, films with thickness between 100 nm and 300 nm have been deposited.

Preparation conditions and thickness values before exposing the samples to analyte are summarized in Table 2. Roughness and thickness were measured by means of a TENCOR profilometer. All these characterizations were carried out in ambient air.

Reflectance VIS spectrum fringes are acquired with S2000 Oceanoptics spectrometer. Thickness was evaluated using an Ocean Optics Nanocalc software [6].

TABLE 2: Summary of the preparation condition and of the thickness values before exposing to gas.

SAMPLE NAME	CB/PHEMA (wt%)	PHEMA/HFiP (wt%)	LAYER THICKNESS PROFILOMETER (nm)	LAYER THICKNESS INTERFEROMETER (nm)
PHEMA_a	0	4	200 ± 30	170 ± 5
PHEMA_b	0	4	250 ± 30	220 ± 5
PHEMA_c	0	4	100 ± 30	140 ± 5
PHEMA/CB_a	5.5	1	250 ± 70	250 ± 5
PHEMA/CB_b	5.5	1	300 ± 70	310 ± 5
PHEMA/CB_c	5.5	1	200 ± 70	200 ± 5

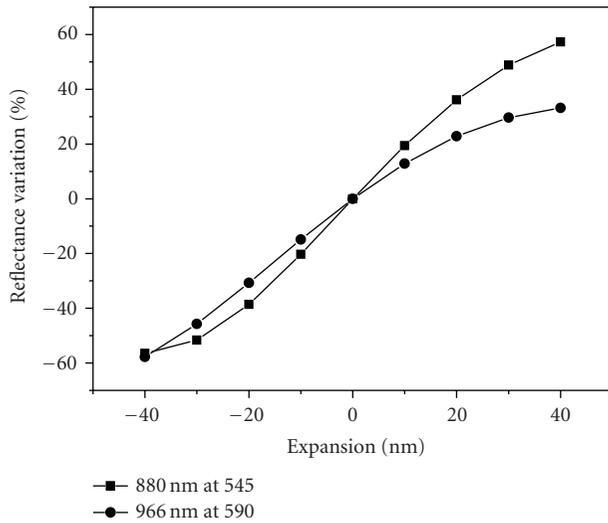


FIGURE 5: Simulated Reflectance variation of PHEMA_b (a) (880 nm thickness at 545 nm), and PHEMA/CB_a (b) (966 nm thickness at 590 nm).

The sensible layers were mounted in the test chamber and analyzed upon VOCs exposure. The experimental setup consists of a small chamber based on a modified multiple tube-fitting connector (Figures 4(a) and 4(b)).

Sample is placed on the top of an adjustable stage (Figure 4(a)-(1)). Fiber optic reflection probes are connected to a VIS-NIR light source through SMA connector and aligned with the sample (Figure 4(a)-(3)). The reflected light beam is collected by the fiber and directed to the spectrophotometer.

Measurements in controlled environment were performed using a Gas Sensor Characterization System better described elsewhere [11] connecting the optical chamber (Figure 4(a)-(2)) to the gas output of the electrical test chamber.

Ethanol at concentration of 3000 ppm and 12500 ppm in N_2 was used as testing analyte. The vapor was introduced in the test chamber by means of a bubbler system in controlled by mass flowmeters amounts. Gas mixture and concentration output (Figure 4(a)-(4)) were finally checked by a Thermo Antaris IGS FTIR gas analyzer.

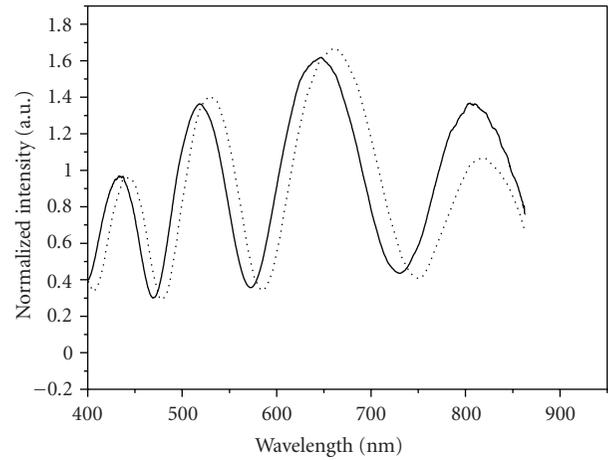


FIGURE 6: Reflected light intensity spectra of PHEMA_b sample under nitrogen (solid line) and exposed to 12500 ppm of ethanol vapors (dotted line).

4. Results and Discussion

As shown in Table 2, the optically evaluated thickness is, within the experimental error, equal to the value determined by the mechanical profilometer, confirming the validity of the employed model. Curiously, the agreement between optically and mechanically evaluated thickness seems to be even better for the nanocomposite rather than for the pure polymer.

The evaluation of the swelling is based on the experimental shift of the reflectance interference pattern at a fixed wavelength, chosen near the inflection point. As previously discussed, according to the model, a swelling of few tenths of nanometers is related to the optical reflectance variation at that wavelength.

In Figure 5, the simulated variations at a fixed wavelength as function of the swelling for the samples PHEMA_b and PHEMA/CB_a, calculated on the basis of (1), are reported. For a given reflectance, the corresponding layer expansion can then be readily evaluated.

Figure 6 shows the shift of interference fringes of PHEMA sample exposed to 12500 ppm of ethanol vapors, where a clearly observable effect of the volume change is detected. Using the outlined model a 19 nm swelling with a 10% confidence was calculated.

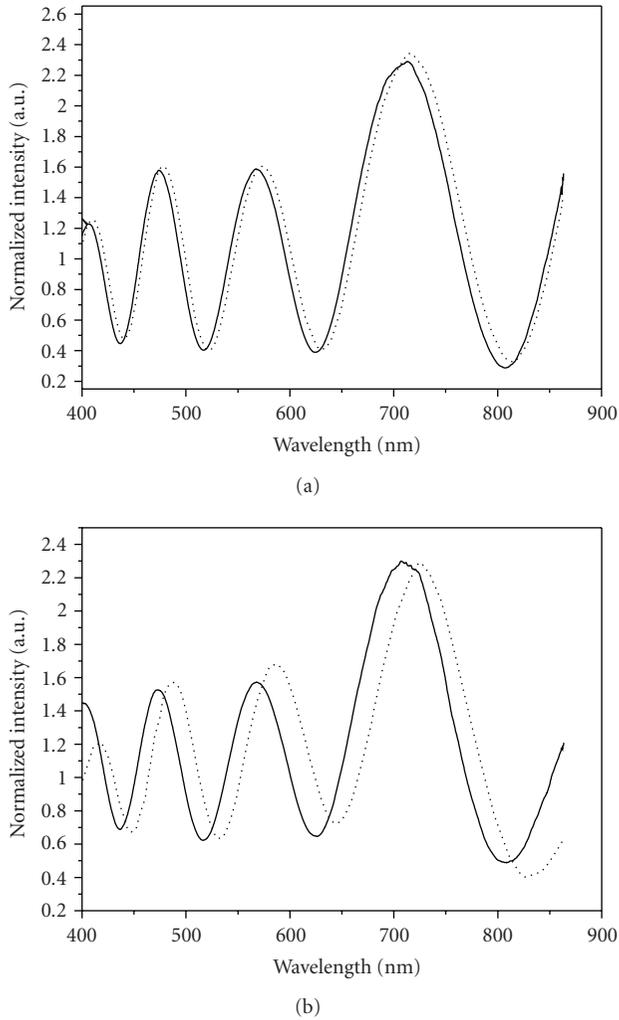


FIGURE 7: Reflected light intensity spectra of PHEMA/CB_a sample exposed to 3000 ppm (a) and to 12500 ppm (b) of ethanol vapors (dotted lines). Reflectance spectra of samples exposed to pure N₂ are shown for comparison (solid lines).

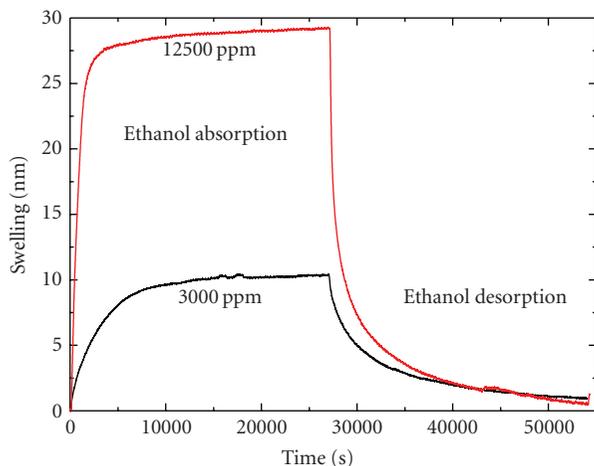


FIGURE 8: Swelling versus time for a PHEMA/CB_a film in 3000 ppm and 12500 ppm of ethanol vapors.

In Figures 7(a) and 7(b), the shifts of interference fringes of the PHEMA/CB_a sample exposed to 3000 ppm and 12500 ppm of ethanol vapors, respectively, are shown. The swelling evaluation gives a thickness variation of 10 nm for the sample exposed to 3000 ppm while an expansion of 31 nm is found when the same sample is exposed to 12500 ppm of ethanol. As expected, the amount of film expansion depends on the concentration of the analyte.

Nanocomposite layers exhibit a slightly larger swelling as compared to pure PHEMA layers. A similar result has been previously observed for nanostructured fluoropolymer (CF_x) and metal-CF_x composite films [12]. A possible active role of the metal filler has been suggested in that case, to account for this effect. In our case, preliminary investigations by means of Brunauer-Emmett-Teller (BET) measurements have highlighted the occurrence of a certain porosity in the nanocomposite with respect to the bare polymer. The enhanced specific surface could then account for the observed swelling.

In Figure 8 the swelling kinetics of PHEMA/CB_a sample recorded at 660 nm, at two different analyte concentrations, is reported. The swelling in presence of 12500 ppm is greater than the expansion related to 3000 ppm exposure. Data exhibit the typical $(t)^{1/2}$ law at least for the first 600 s. During this time interval a diffusive mechanism can be then assumed and, using the Fick equation, the diffusion coefficients can be estimated. For PHEMA exposed to 12500 ppm of ethanol the evaluated diffusion coefficient is equal to 1×10^{-14} cm²/s, while the diffusion coefficients for PHEMA/CB exposed to 3000 ppm and 12500 ppm of ethanol are 1×10^{-16} cm²/s and 0.5×10^{-14} cm²/s, respectively. Data for pure PHEMA are comparable with those reported by Goustouridis et al. [3].

5. Conclusions

In this work, we developed a simple optical method based on thin film white light interferometry to measure the swelling sensitivity of polymer and nanocomposite layers. The method allows to easily correlate polymer nanocomposite film expansion to light intensity variation at a fixed wavelength, as long as the swelling is small with respect to the whole layer thickness.

It was successfully applied to PHEMA and to nanocomposite carbon black/PHEMA layers which are a typical choice in chemical sensor technology. Interestingly, we have found that the nanocomposite undergoes a more pronounced swelling process with respect to pure polymers.

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