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A Study of the Swelling Properties of Polymer Nanocomposites through Electrical and Optical Characterization

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Summary: In the present study, polymer nanocomposite layers for sensing applications are characterized by means of an optical method based on white light interferometry. The study focuses on poly (hydroxy ethyl methacrylate) (PHEMA) and on nanocomposite Carbon black (CB)/PHEMA layers commonly used in chemical sensor technology for volatile organic compounds (VOCs) detection. The interferometric spectra of these two different materials, recorded during analyte exposure, are analyzed in terms of film expansion. Comparison between PHEMA and PHEMA/CB layer shows that the nanocomposite undergoes a more pronounced swelling process. In order to achieve a better comprehension of the sensing mechanism and to improve the sensor performances, the variations of the electrical signal of a nanocomposite-based chemiresistor in presence of VOCs are examined and compared to the optical behaviour.

Keywords: chemical sensors; interferometry; swelling

Introduction

Polymer films and their nanocomposites, consisting of inorganic nanoparticles, such as carbon particles, 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] These chemical sensors work on the basis of a change of their electrical properties when they come into contact with a specific substance. This mechanism is associated to the polymer matrix volume change due to the solvent absorption (swelling),[2–4] and to the corresponding reduction of the carbon particles volumetric fraction.[5] The change in film volume results in a modification of the conduction paths through the film measured as a change in resistance across the film.

Among the polymers, the PHEMA is very interesting in the sensor field for the easy processability and for its hydrophilic properties.[6] Goustouridis et. al analyzed the PHEMA expansion, absorption/desorption kinetics and selectivity in the presence of two volatile organic compounds (methanol and ethanol) as a function of the thickness of the polymer.[3]

The inclusion of CB into PHEMA allows to modify and tune polymer electrical properties by varying the concentration of the incorporated inorganic part. An exhaustive study on the nanocomposite-based sensors has been carried out by Ryan et al.[1] in a paper focused on the optimization of the sensing films fabrication process to increase the sensitivity of an array for e-nose.

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In this work, the swelling of polymer and nanocomposite layers is analyzed using an optical method based on white light interferometry. The study focuses on PHEMA and on a nanocomposite carbon black/PHEMA layer which is a typical choice in chemical sensor technology.[2,3,6,7] The optical response of these polymeric layers upon exposure to solvent vapours is investigated in terms of film expansion. In addition, electrical signal changes in presence of solvent vapours are examined and compared to the optical behaviour in order to achieve a better comprehension of the sensing mechanism and to improve the sensor performances.

Experimental Part

The PHEMA series of samples were prepared by dissolving the polymer (4 wt%) in hexafluor-2-propanol (HFiP), while the PHEMA/CB layers were made dispersing carbon black (5.5 wt%) in the PHEMA (1 wt%)/HFiP solution. After sonication the solutions were spin-coated on crystalline Si wafers, where a 600 nm thick SiO_2 layer has been previously e-beam evaporated. Preparation condition and thickness values before exposing the samples to gas are summarized in Table 1.

According to the theoretical study film thickness has been chosen in order to maximize the number of interferometric fringes and to optimize the conditions for the shift study. The layers were mounted in the test chamber and analyzed during VOCs exposure. The experimental setup consists of a small chamber based on a modified multiple tube-fitting connections (Figure 1a and 1b).

The chamber is placed in a thermostatic box (Figure 1c) at controlled temperature and humidity.

The samples are placed on the top of a screw adjustable stage. Fiber optic reflection probes (connected to a VIS-NIR light source through SMA connector) is aligned with the sample. The reflected light beam is collected by the fiber and directed to the spectrophotometer (Ocean Optics S2000). VOCs are introduced by means of a dry nitrogen flow in an amount controlled by mass flow controllers.

An interdigitated Au structure was deposited on a PHEMA/CB sample by e-beam evaporation; such chemiresitor was electrically characterized before and during vapour exposure.

In order to investigate the PHEMA/CB films, a Dual Beam (FEI Quanta 200 3D) was used for evaluating the CB dispersion and for controlling humidity influence. Dual Beam consists of a Environmental Scanning Electron Microscope (ESEM) and a Focused Ion Beam (FIB). ESEM offers the possibility of imaging insulating materials under water vapour. FIB, instead, uses a highly focused and energetic Ga ions which raster sample surface and induce ion secondary electrons (ISE). The contrast mechanism for ISE generation offers information about surface and composite morphology.

Optical Model

The film expansion can be calculated starting from the interference equation.[8] Due to the small concentration of the analyte the samples are exposed to, the material index can be assumed as constant

Table 1.
Summary of the preparation condition and of the thickness values before exposing to gas.

Sample name	CB:PHEMA (wt%)	PHEMA:HFiP (wt%)	Nominal layer thickness (nm)	Layer thickness by 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

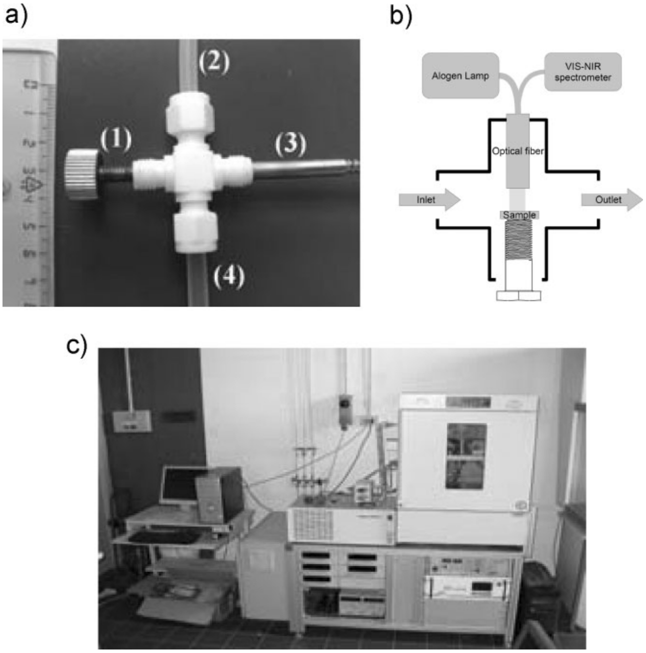

Figure 1.
photograph (a) and scheme (b) of the chamber for optical characterization in controlled environment: (1) sample holder, (2) gas inlet, (3) fiber optic holder, (4) gas outlet; (c) experimental apparatus.

at different wavelength even during vapour absorption. We have verified that the refraction indeces of the PHEMA and PHEMA/CB differ only by a few percent, and both are very similar to the SiO_2 index ($n(SiO_2) = 1.45$ and $n(\text{PHEMA or PHEMA/CB}) = 1.51$). That implies that system composed by SiO_2 and PHEMA (or PHEMA/CB) layer can be simplified and treated as single layer.

Therefore, the total reflection of light beam impinging on a substrate covered by a single non absorbing layer whose thickness is d_1, can be assumed equal to:

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

where r_i is the reflectance between the (i-1)th and ith layer, given by

$$r_i = \frac{(n_{i-1} - n_i)}{(n_{i-1} + n_i)} \quad i = 1,2 \qquad (3)$$

θ is the phase thickness of the coating

$$\theta = \frac{2\pi n_1 d_1}{\lambda} \qquad (4)$$

n_0, n_1 and n_2 are respectively the air, the layer, and the substrate refractive indices. The reflectance minima occur when:

$$n_1 d_1 = k_n \lambda_0 / 4 \qquad (5)$$

where k_n is the order of the minimum and is an odd integer. In presence of an analyte the optical path $n_1 d_1$ in the film changes and a shift of the position of the maxima and minima occurs. The evaluation of the swelling, that is the variation of layer thickness (d_1), is based on the experimental shift of the maxima and minima and is calculated using the equation (5); the order of the maximum (k_n) is determined analyzing the interference fringes of the SiO_2 layer before depositing the polymer or the nanocomposite film on it.

Results and Discussion

The shifts of interference fringes of PHEMA_b sample exposed to 12500 ppm of ethanol vapours are depicted in Figure 2,

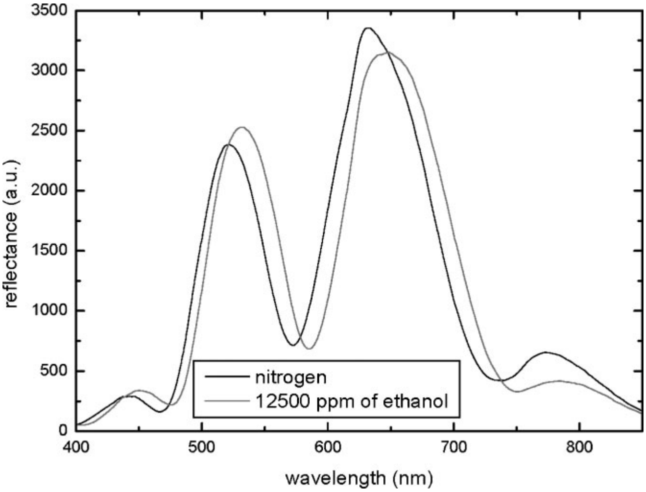

Figure 2.
Reflectance spectra of PHEMA_b sample under nitrogen and exposed to 12500 ppm of ethanol vapours.

where a clearly observable effect of the volume change is evident. The swelling in this case is equal to 19 nm.

Carbon black dispersion in the nanocomposite and the morphology of the film has been investigated by ESEM/FIB technique. In Figure 3, an image of the PHEMA/CB_a sample, examined by FIB is reported. Homogeneously dispersed agglomerates, with dimensions ranging from 30 nm to 220 nm, were observed into the polymer layer with no apparent dependence on the surface distance. No evident morphological change of the nanocomposite surface occurs after water vapour introduction at room temperature during the ESEM analysis.

In Figure 4a and 4b the shifts of interference fringes of the PHEMA/CB_a

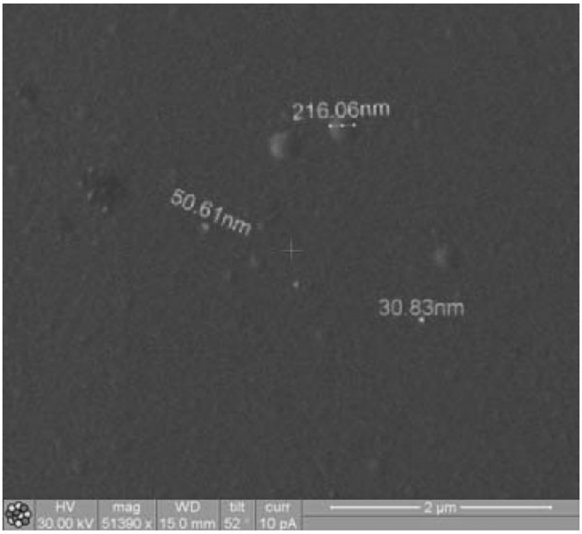

Figure 3.
Ion image of PHEMA/CB_a layer. Different sized Carbon Black particles are evident.

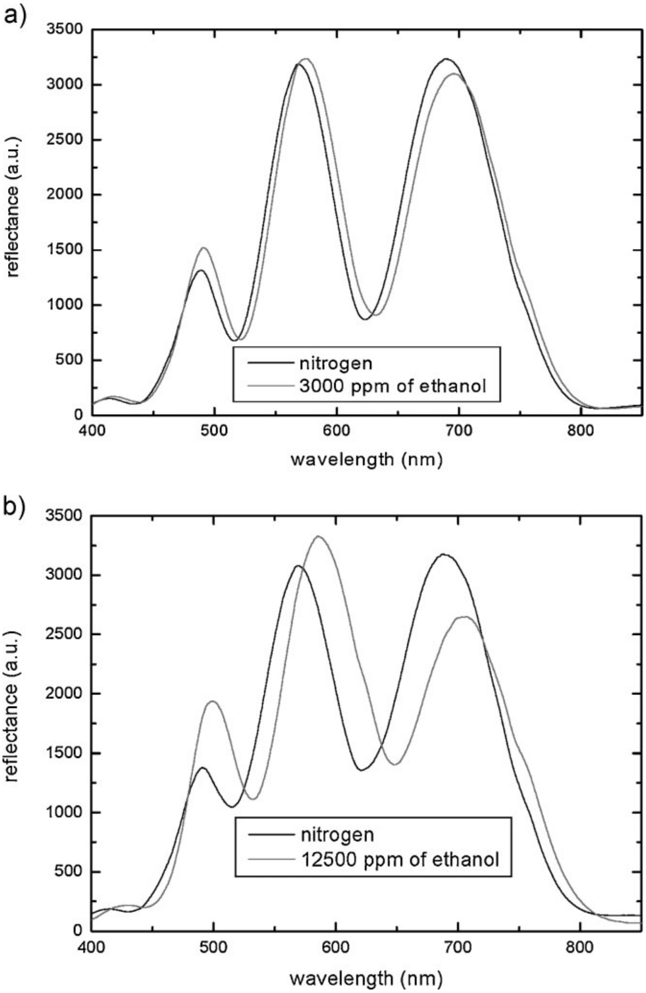

Figure 4.
Reflectance spectra of PHEMA/CB_a sample exposed to 3000 ppm (a) and to 12500 ppm of ethanol vapours (b) compared to the spectra in nitrogen.

sample exposed to 3000 ppm and 12500 ppm of ethanol vapours respectively are shown. The analysis of the fringe shift gives a thickness variation of 10 nm for the sample exposed to 3000 ppm while an expansion of 29 nm is found when the same sample is exposed to 12500 ppm of ethanol. We can observe that the amount of film expansion depends on the concentration of the analyte; similar results were also found by Goustouridis and coworkers.[3]

Nanocomposite layer exhibits a slightly larger swelling compared to the simple PHEMA layer. An analogous result was reported in a comprehensive study on the swelling properties of a particular class of polymer nanocomposite,[9] composed of fluoropolymer (CF_x) and metal. There was observed that the swelling sensitivity increases by the inclusion of metal nanoparticles in the polymer matrix. Physical permeation of the vapour through material pores has been excluded as explanation of the phenomenon, while a key role has been ascribed to the formation of analyte–Me_{ox} complexes in the swelling process. A similar effect could also occur in the case of carbon-based nanocomposite, but currently we have no enough elements to confirm this hypothesis, and the elaboration of a general model that describes the material–vapour interaction, applicable also to a larger class of nanocomposite materials is beyond the aim of this study.

Since the layer swelling is very small with respect to its total thickness a linear relationship between the reflectance variation and the fringe shift can be assumed:

$$\Delta d_1(t) = \alpha R(t)$$

The time evolution of the optical reflectance at a fixed wavelength can be then readily correlated to the swelling kinetic.

In Figure 5 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 three times greater than the expansion relative to 3000 ppm exposure.

The adsorption and desorption kinetics allows to estimate the diffusion coefficients. In a polymer film displaying a purely fickian diffusive regime, the diffusion coefficient D for long time values exhibits a square root dipendence over the time, and is correlated to the total amount of vapour absorbed at time t (M), to the equilibrium sorption value (M_∞) and to the film thickness (d_1) through the following relationship[10]:

$$\frac{M}{M_\infty} = \frac{4}{d_1}\left(\frac{Dt}{\pi}\right)^{1/2}.$$

The diffusion coefficients can be evaluated from the slope of the curve obtained plotting the M/M_∞ ratio, or equivalently the thickness variation normalized to the final value, against the square root of time, since a linear relationship between d_1 (t) and M (t) can be assumed.

In Table 2 the values of the calculated diffusion coefficient of the polymer and nanocomposite films are reported. The observed values are consistent with the PHEMA diffusion coefficient reported in the literature.[3] A difference of a factor two is observed between PHEMA and PHEMA/CB exposed to 12500 ppm, and a dependence on the analyte concentration of the

Table 2.
PHEMA and PHEMA/CB diffusion coefficients in ethanol at different concentrations.

Sample	Diffusion coefficient in ethanol (3000 ppm)	Diffusion coefficient in ethanol (12500 ppm)
PHEMA_b	–	2×10^{-13} cm^2/s
PHEMA/CB_a	1×10^{-14} cm^2/s	0.8×10^{-13} cm^2/s

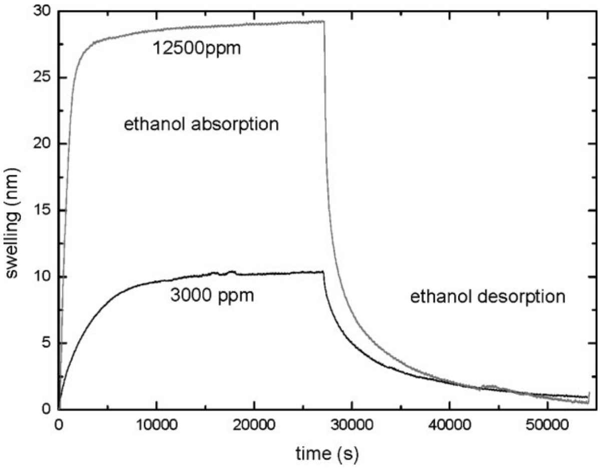

Figure 5.
Swelling vs. time PHEMA/CB_a film in 3000 ppm and 12500 ppm of ethanol vapors.

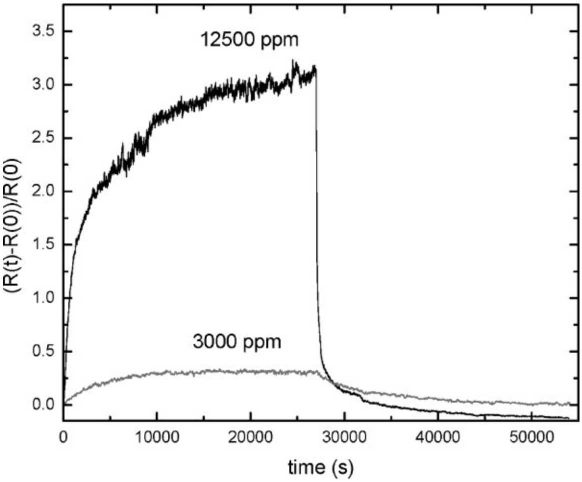

Figure 6.
Electrical responses of PHEMA/CB_a sample sensing film in 3000 ppm and 12500 ppm of ethanol vapors.

diffusion coefficient for PHEMA/CB is evident. The dependence of the PHEMA diffusion coefficient on the concentration of VOCs, although less pronounced, was also observed by Goustouridis and coworkers.[3] However this is the first time that such an effect is observed in a nanocomposite.

In Figure 6 the results of PHEMA/CB_a sample electrically characterized upon exposure to 3000 and 12500 ppm of ethanol vapours are reported.

The difference in optical and electrical responses over the time (Figure 5 and 6) suggests that different mechanisms could determine the optical and electrical behaviours. In the latter case the swelling phenomenon does not involve only the surface of the layer, but the external analyte could deeply penetrate into the film, disrupting the electric paths in such a way to strongly modify the device conductance.

Conclusion

In this work we have compared the swelling sensitivity of PHEMA and PHEMA/CB, commonly used in chemical sensor technology for VOCs detection, verifying that the nanocomposite undergoes a more pronounced swelling process. We have also investigated the swelling and the electrical kinetics of the PHEMA/CB. No linearity between the film swelling and its electrical behaviour has been found; the VOCs adsorption results in a strong effect on the electrical response, suggesting that the measured swelling is the average result of the analyte penetration in the whole layer.

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