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Real time investigation of swelling kinetics and electrical response in polymer nanocomposite based chemical sensor

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Abstract

Swelling is generally assumed to be the key operating mechanism in polymer nanocomposite chemical sensors.Here the swelling kinetics has been correlated to the sensor electrical performances. In this study, poly(2-hydroxyethyl methacrylate)/ carbon black nanocomposites have been deposited on silicon or alumina substrate and have been used as sensing layer for conductive chemical sensors. A kinetics study of the device swelling characteristic and of the electrical response to ethanol vapors was performed. Filler structure and morphology have been found to differently affect the polymer nanocomposite swelling behavior. Results are used to optimize sensing layer fabrication and thus improve sensor performances.

Keywords: chemical sensors; swelling; interferometry

1. Introduction

Gas sensing properties of conductive polymer nanocomposites have been extensively employed in fabricating chemical sensors, vapor detector arrays and electronic noses. Upon solvent vapors exposure they undergo a reversible change in electrical resistance. In particular, carbon black filled polymer composites work on the basis of percolation theory. Since the swelling phenomenon is considered to be the key mechanism responsible for the change in resistivity of the sensing material, an in-depth study of the swelling properties of polymer nanocomposites could be beneficial for the optimization of the gas sensor devices. Ryan et al. have deeply investigated the fabrication process of the nanocomposite-based sensors in order to improve the sensitivity of the sensing films [1]. Several amorphous polymeric composites have been synthesized by Zhang and colleagues and their vapor adsorption behavior and its influence on the gas sensitivity have been studied [2]. Goustouridis and coworkers have proposed a method based on white light interferometry for the evaluation of the swelling of non-scattering materials [3]. Nevertheless, a quantitative analysis of the effect of solvent-nanocomposite interaction is still lacking especially as far as the effect of filler properties on sensing films characteristics and hence, on device performances is concerned. Device optimization needs a comparison between electrical response and film expansion under VOCs exposure. In previous work we reported on the implementation in a Gas Sensor Characterization System (GSCS) of

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white light interferometry setup to evaluate the nanocomposites film expansion [4]. That method has been successfully applied to the swelling evaluation of nanocomposite sensing layers fabricated with different carbon black content and deposited on different substrates and to their real-time correlation with device behavior. Various films morphology, due to different filler types (such as carbon nanotubes single and multi-walled) and content, could be correlated to the swelling behavior and electrical responses of sensor devices upon ethanol vapors exposure. In the next pages some preliminary results on PHEMA (poly(2-hydroxyethyl methacrylate))/Carbon Black (CB) sensor devices with different filler content are reported.

2. Experimental

The PHEMA series of samples were prepared by dissolving the polymer (1 wt%) in hexafluor-2- propanol (HFiP), while the PHEMA/CB layers were obtained by dispersing carbon black Pearls® 2000 (CABOT Corporation) in the PHEMA/HFiP solution at concentrations ranged from 0 to 10 wt% with respect to polymer. The carbon black content is determined on a weight basis of the components in the starting dispersion. Characterizations by means of Thermogravimetric Analysis (TGA) on PHEMA/CB nanocomposite films have shown that the weight ratio, polymer/filler, in the dispersion is preserved in the deposited film. CB size distribution were determined by Dynamic Ligth Scattering (DLS) by means of Malvern HPPS-ET Standard System. After sonication, the solutions were spin-coated at 5000 rpm on SiO_2 coated crystalline Si wafers. For this study films with thickness between 200nm and 300nm have been deposited. Roughness and thickness were measured by means of a TENCOR profilometer. Films morphologies were investigated using an optical Polyvar MET by Rechert-Joung microscope. All these characterizations were carried out in ambient air. Reflectance VIS spectrum fringes are acquired with S2000 Oceanoptics spectrophotometer. 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 (fig. 1a and 1b). Sample is placed on the top of an adjustable stage (fig. 1a-1). Fiber optic reflection probes are connected to a VIS-NIR light source through SMA connector and aligned with the sample (fig. 1a-3). The reflected light beam is collected by the fiber and directed to the spectrophotometer. Measurements in controlled environment were performed using a GSCS better described elsewhere [5] connecting the optical chamber (fig. 1a-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 amounts controlled by mass flowmeters. Gas mixture and concentration output (fig 1a-4) were finally checked by a Thermo Antaris IGS FTIR gas analyzer.

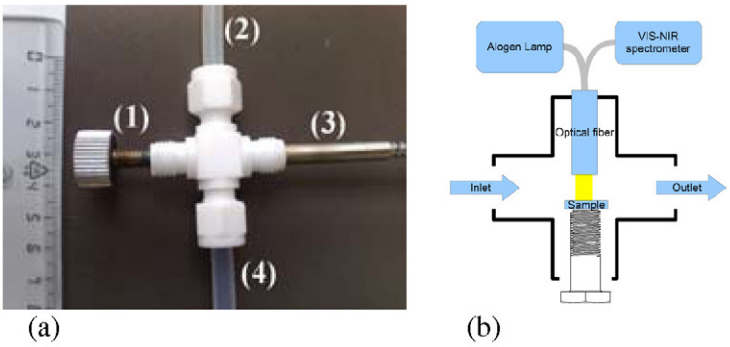

Fig. 1: (a) photograph of the chamber for optical characterization in controlled environment: (1) sample holder, (2) gas inlet, (3) fiber optic holder, (4) gas outlet; (b) a scheme of the chamber for optical characterization.

3. Res ults and discussion

In table 1 are summarized the results of DLS and profilometer characterizations. CB incorporation enhances the surface roughness. Optical investigations confirm the roughness increment with CB content.

Table 1: Summary of the DLS and profilometer characterizations on PHEMA/CB nanocomposites.

CB percentage in PHEMA (wt %)	Mean CB particle size (nm)	Thickness (nm)	Roughness (nm)
0	-	170-250	3-5
5	780	270-320	6
10	660	240-280	20

In fig.2 some optical micrographs of PHEMA/CB nanocomposite films, at increasing filler content are shown. The carbon particles are homogeneusly dispersed in the polymer matrix; as it was previously seen by DLS analysis of the starting dispersions. PHEMA/CB 5% nanocomposite film (fig.2b) shows larger carbon aggregate size and minor particle density with respect to PHEMA/CB 10% nanocomposite film (fig.2c). In fact, the impedance of the device realized by depositing interdigitated electrodes (see fig.3) on nanocomposite films are 6.5 MΩ and 35 kΩ respectively for PHEMA/CB 5% and PHEMA/CB 10%.

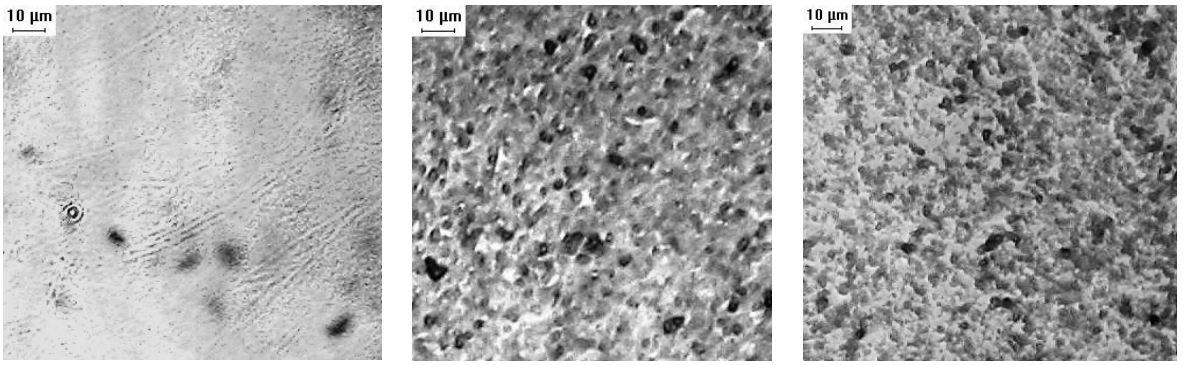

Fig. 2: Optical micrographs of PHEMA/CB films deposited on Si/SiO_2 substrate: (a) bare PHEMA film; (b) PHEMA/CB 5% film; (c) PHEMA/CB 10% film.

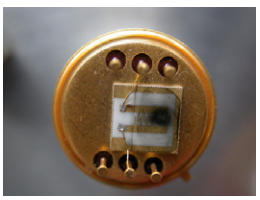

Fig. 3: Photograph of PHEMA/CB 10% sensor devices fabricated Al_2O_3 substrate.

In fig.4 the linearity between electrical response and swelling behavior for the nanocomposite film with 5% of carbon black is evident.

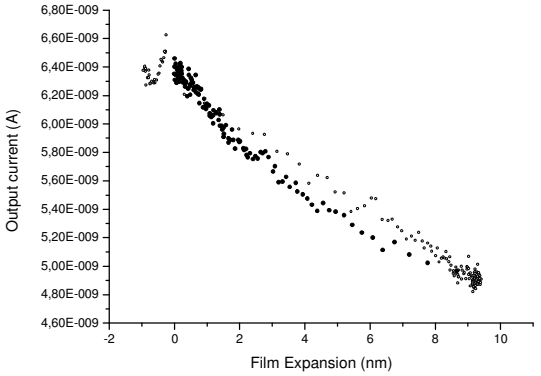

Fig. 4: Electrical Response Vs. Swelling in PHEMA/CB 5% sensor device when exposed to ethanol at 6000ppm and biased with 1V DC.

Conclusions

It has been shown that optical interferometry can be used to real time measuring the swelling in carbon black polymer nanocomposites. Increasing the carbon black concentration, percolation occurs for PHEMA/CB concentration greater than 10 wt%. The amount of swelling can be readily correlated to device electrical response. This investigation allows the improvement of the device performances by correlating absorption kinetics and sensor device electrical response.

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