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Understanding the sensing mechanism of polyaniline resistive sensors. Effect of humidity on sensing of organic volatiles

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ABSTRACT

Polyaniline (PANI) is the oldest and potentially one of the most useful conducting polymers. Among other technological applications, PANI films have been extensively used as resistive sensors of volatile analytes. However, at present the mechanism underlying the resistivity changes of the films upon exposure to volatile substances is still unclear. In this work, we investigate different effects of the volatile absorption which can cause the changes polymer electrical resistance when it acts as resistive sensor. This model takes into account three major components: (i) changes in the electronic structure of the polymeric chains (ΔR_{ele}), (ii) variations in the electron hopping process (ΔR_{hop}) and (iii) changes in the ionic conductivity between chains due to changes in the dielectric medium between them (ΔR_{med}). Using two point probe resistivity, UV–visible spectroscopy, environmental ellipsometric porosimetry and atomic force microscopy we study the effect of volatiles on polyaniline films properties to improve the understanding on the mechanism of resistivity changes. Specifically, in the case of water absorption, the resistivity changes seem to be associated with dielectric medium changes and swelling effects (in the high humidity range). It is found that ambient humidity not only gives a resistive signal but also strongly affect the sensing of other volatiles (e.g. ethanol).

1. Introduction

The market of chemical sensors continues growing at a rapid rate, reflecting the wide range of possibilities of improving technological processes within the industrial, agricultural, military sector, among others [1–7]. Recent advances in polymer science and films preparation have made polymer films useful, practical and economical for wide range of sensing applications. Classical polymers are dielectric, so they have to be mixed with conducting materials (e.g. carbon particles) to build electric sensors based on changes of conductivity. However, pure conducting polymer films can be directly used in this kind of sensors. Among them, polyaniline (PANI) is one of the more interesting conducting polymers, which is a suitable material to produce chemical sensors, due to its processability, high sensitivity and low cost [8]. The development of efficient chemical sensors is challenging and a lot of work is in progress to explore new materials with improved sensing characteristics [9–14].

In the literature there are many research works about sensors built using conducting polymers. S.V. Bhoraskar et al. [15] reported the behavior of humidity sensors with polyaniline-based conducting polymers doped with different weak acidic, Lau et al. [16] described the use of polyaniline nanofibers as an humidity sensor. In both cases, PANI is the sensitive material used and the authors proposed that the humidity sensing mechanism can be explained on the basis of proton transfer mechanism. Kulkarni et al. [17] have also studied PANI and modified PANI as humidity sensors, and Varahramyan et al. [18] have shown that the use of layer-by-layer nano-assembly for deposition of ultrathin poly(anilinesulfonic acid) films in order to fabricate highly sensitive and fast responsive humidity sensors. However, none of these

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Table 1
Relationship between relative humidity and sulfuric acid concentration.

Concentration of sulphuric acid solutions (mol/l)	Relative humidity (%) at 20 °C
0.0	98.0
4.3	70.4
6.0	47.2
9.2	18.8
18.7	3.2

works have been focused on the interaction mechanism involved when the sensitive material is in contact with the analyte molecule.

Resistive PANI sensors have been applied in different fields [19]. The effect of humidity on the volatile's signal, described in the present communication, have to be taken into account in those applications.

In this paper we employ different techniques: two point probe, atomic force microscopy, UV–visible spectroscopy and environmental ellipsometric porosimetry to study the processes involved in the polymer–analyte interaction while the PANI changes its resistivity. Based on these results, we propose a model that explains the changes on the electrical resistance of the polymer when this acts as resistive sensor. The model takes into account three components: (i) the intrinsic resistivity of the polymeric chains due to electronic effects (ΔR_{ele}), (ii) the resistivity changes related to variations in the electron hopping process (ΔR_{hop}) and (iii) the resistivity changes due to modifications in the dielectric medium between the chains (ΔR_{med}). Moreover, we applied successfully the proposed model to explain how changes in ambient humidity alters PANI sensor readings when sensing butanol or ethanol.

2. Materials and methods

2.1. Sensor fabrication

The resistive sensor was made using a polymeric inert support (polyester woven cloth) covered with PANI as a sensitive material. To study the main processes involved in the characteristic response of the PANI, different supports were used, such as polypropylene (PP), polyethylene (PE) or gold slides (emf®). The conducting polymer was deposited onto these supports by in situ polymerization, which involves chemical oxidation of aniline (0.1 M) in HCl (0.1 M) with ammonium persulphate (equimolar to aniline) at 0 °C. This procedure has been previously described in detail in literature [20–22]. The polymerization reaction was performed in a glass vessel reactor with 400 ml of capacity, and cooled with an ice-water bath at 0 °C. The reaction temperature was measured using a thermocouple (Hanna Instruments) with an accuracy of 0.1 °C. After the polymerization, PANI covered supports were washed with HCl 1 M and dried at ambient conditions.

Once the sensitive material onto polyester woven cloth was dry, a piece of 1.5 cm × 1 cm was cut and then electrically contacted. The sensors supported on PE and PP were cut into 0.5 cm × 1 cm pieces.

2.2. Control of ambient humidity

To control the relative humidity (RH), different solutions of sulphuric acid were used [23]. The RH and the equilibrium vapour pressure used for the present experiments are given in Table 1.

2.3. PANI film characterization

2.3.1. UV–visible spectroscopy

UV–visible spectra of the PANI films deposited onto PP commercial films were measured in transmission mode using a HP 8452 UV–visible Spectrophotometer. Films were placed inside a stoppered quartz cell and the RH inside the cell was stabilized with aqueous solution of sulfuric acid (see Table 1).

2.3.2. Scanning electron microscopy (SEM)

The polymer was deposited onto polyester woven cloth by in situ polymerization and then the morphology of the films was studied using a Carl Zeiss EVO MA 10 low vacuum scanning electron microscope.

2.3.3. Fourier transform infrared spectroscopy (FTIR)

FITR spectra were obtained using a Bruker Tensor 27 FTIR spectrometer with a resolution of 4 cm^{-1}. The spectrum of the conductive polymer supported onto PE was obtained in transmission mode. The PE film was pretreated with sulfochromic solution to produce hydrophilic groups on the film surface before polymerization.

2.3.4. Environmental ellipsometric porosimetry (EEP)

EEP technique, first reported by Baklanov [24] is a very powerful technique for studying the evolution of thickness and refractive index of supported thin films at different humidity conditions. The experimental device is based on the coupling of a pressure controlled chamber and a variable angle spectroscopic ellipsometer. Film thickness and refractive index values were obtained from the ellipsometric parameters φ and Δ [25] under nitrogen flux with a variable water content, reaching RH values from 0 to 90%. This technique is usually used to study porous oxide films [26] but can be adapted to evaluate polymer swelling [27]. EEP measurements were performed using a SOPRA GES5A spectroscopic ellipsometer.

To model the ellipsometric signal, the Cauchy model and two Lorentz peaks were used. The refractive index n and $k(\lambda)$ values reported by Barbero et al. [28] for this material were used as seeds. The refractive index curves obtained can be found in the Supplementary Information (Fig. S1). The initial thickness of the used polymeric film was 150 nm, which was measured using an Atomic Force Microscopy Agilent 5500.

2.3.5. Atomic force microscopy (AFM)

AFM measurements were made with an Agilent 5420 AFM/STM microscope in contact mode with a commercial Point Probe® Plus Contact/Tapping Mode (constant force of 6 N m^{-1}, 156 Hz) It allowed the determination of the change in thickness of the PANI film as it passes from a protonated state to a deprotonated state. The polymer was deposited onto a gold slide by in situ polymerization. Then, a single laser pulse (532 nm, 350 mJ/cm^2, 6 ns pulse width) was used to remove a part of polymeric material and a circular hole was made on the polymeric film. Fig. 1 shows a covered and an uncovered area. The height changes suffered by the polymeric film after being exposed to acid and basic solutions were measured.

2.3.6. Conductometric response of the sensors

To study the effects of humidity on sensor response, the sensor was placed on the top of different closed Erlenmeyers (250 ml). The RH value in each Erlenmeyer was obtained using sulphuric acid solutions at 20 °C, as previously described. The sensor was placed for 20 min on the top of Erlenmeyer with the lowest humidity. Then, the sensor was changed to the sample flask (ethanol, butanol, etc.) for 20 min and the electrical response was recorded. In this static set-up, the equilibrium conditions are achieved. After that, the sensor was placed for 20 min in the second Erlenmeyer that contained 18.8% RH, and then was changed again for 20 min to the sample flask and so on.

The sensor response was measured with a multimeter (Kaiser, VA 40B). The two probe method was used to perform the

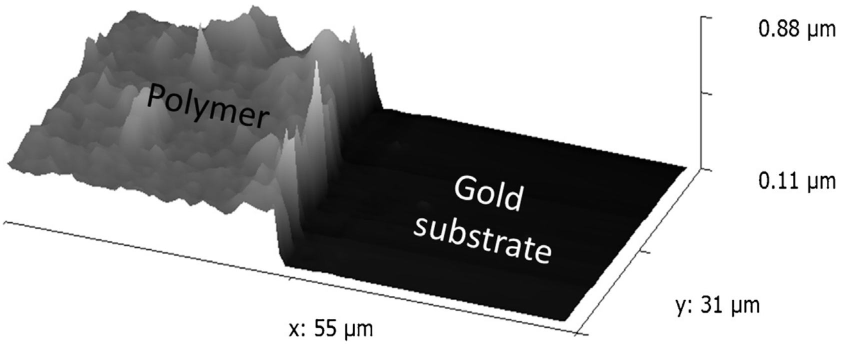

Fig. 1. AFM image of PANI onto gold slide.

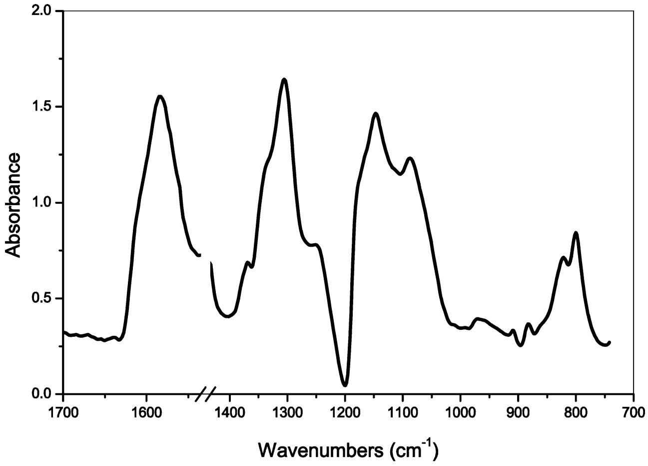

Fig. 2. FTIR spectrum of PANI in conductive form.

measurements. The value S (%) is defined as the relative change in the electrical resistance using the follow equation:

$$S(\%) = (R - R_0) \times \frac{100}{R_0} \quad (1)$$

where R_0 is the initial resistance and R is the resistance value at a certain time.

3. Results and discussion

3.1. Characterization of polyaniline

PANI obtained onto PE was characterized by FITR spectroscopy. Fig. 2 presents the spectrum of PANI and Table 2 shows the characteristic absorption bands of the polymer [29,30].

The peak located at ca. 1490 cannot be seen clearly because PE films have a high absorption around this wavelength. From the analysis of Fig. 2 it is possible to verify the structure of the compound without the necessity of using other methods for further characterization [31].

Table 2
Characteristic bands of PANI.

Wavelength [cm^{-1}]	Bonding	Vibrational mode
1590	C=N	Quinonoid ring stretching
1490	C=C	Aromatic ring stretching
1300	C—H	Stretching
1240	C—N	Stretching
1160	C—H	Bending in plane
820	C—H	Bending out of plane

Fig. 3 shows a SEM image of PANI deposited onto polyester woven cloth.

3.2. Resistive response of the PANI sensor

The electrical response (ΔR_T) of the sensor can be divided in three factors: (i) the changes in the intrinsic resistivity of the polymeric chains due to electronic effects (ΔR_{ele}), (ii) the resistivity changes related to variations in the electron hopping process (ΔR_{hop}) and (iii) the resistivity changes due to modifications in the dielectric medium between the chains (ΔR_{med}). Then,

$$\Delta R_T = \Delta R_{ele} + \Delta R_{hop} + \Delta R_{med} \quad (2)$$

ΔR_{ele} is mainly affected by partial electron transfer between the adsorbed molecule and the polymer chains while ΔR_{hop} by the swelling process that tends to separate the polymeric chains. Finally, ΔR_{med} depends on the dielectric constant of the medium around the chains. The ionic conductivity of an electrolyte is directly related to the dielectric constant of the solvent due to changes in ion stabilization and ion mobility. Therefore, the ionic conductivity contribution will increase with an increasing dielectric constant.

A change in the electronic properties of polyaniline is related to a change in the energy of the optical transitions. This behavior is shown as a shift in the maximum of the position of the spectral band [32,33]. The UV–visible spectrum of PANI deposited onto PP was examined at both low and high RH values (Fig. 4A) and also in presence of some organic vapors (Fig. 4B). As it can be seen, the humidity and the organic vapors (alcohols, ketones and alkanes) have a negligible influence on the spectrum, suggesting that the

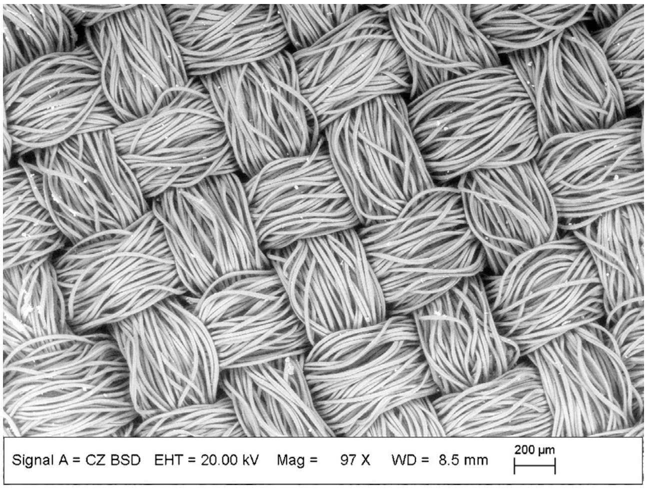

Fig. 3. SEM image of PANI onto polyester woven cloth.

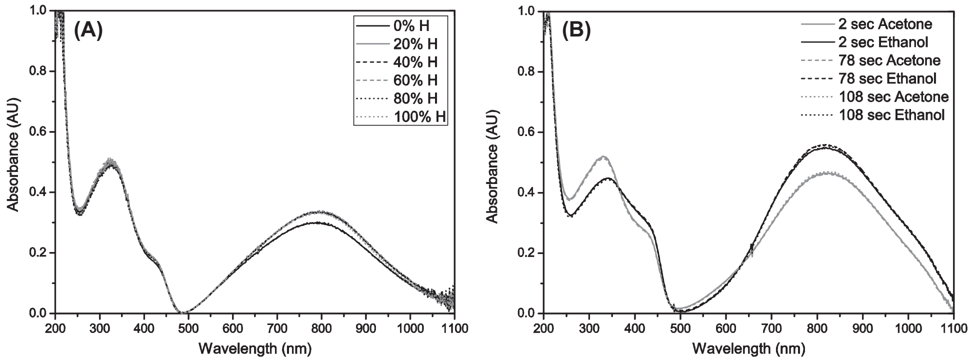

Fig. 4. (A) UV–visible spectra of a PANI film exposed at different RH values. (B) UV–visible spectra of a PANI film exposed at different organic vapors measured at different exposure times.

electronic properties are not affected. The film showed no conformational or doping change when the polymer interacts with these organic molecules. Taking these results into account, we propose that the first term of Eq. (2) (ΔR_{ele}) is negligible and the total resistance in these conditions can be described by Eq. (3).

$$\Delta R_T = \Delta R_{hop} + \Delta R_{med} \tag{3}$$

Therefore, the exposure of the sensor to an analyte the total resistance, which depends on the dielectric constant of the analyte and the swelling effect that the analyte can produce on the PANI film. However, it is known that the electronic properties of PANI are highly dependent on pH [31]. At acid pH, the maximum of UV–visible absorption due to polarons and bipolarons is at ca. 800 nm (green films), and the film is conductive due to the large concentration of free carriers (polarons). At basic pH, the polymer presents a maximum of UV–visible absorption at ca. 600 nm (blue films), and behaves like an insulating material [34]. These results are in complete agreement with our data, as it can be seen in Fig. 5. Such changes only occur when PANI interacts with acidic or basic vapors. In that case, the first term of Eq. (2) cannot be neglected.

Moreover, when the polymeric material changes from insulator to conductive form, it suffers a change in its volume; this effect was measured by AFM. Fig. 6 shows that the polymer changes its height by 30%. This value is in concordance with values previously reported by other authors [28,35].

In order to study the polymer behavior during the water absorption–desorption process, the EEP technique was used. Fig. 7A shows that the polymer refractive index n (measured at $\lambda = 630$ nm) increases linearly with RH. This indicates a continuous adsorption of water within the polymer structure because the refractive index of water at $\lambda = 630$ nm (1.332) is higher that the refractive index of the polymer (1.225, measured at 0% RH). Fig. 7B shows how thickness is dependent on the RH. For RH values lower than 65%, the polymer film does not present thickness changes, indicating that no swelling occurs. On the other hand, for a humidity level above 65%, the polymer film starts to swell and the thickness increases, reaching an increment of around 10% at RH 90%.

As previously mentioned, the continuous adsorption of water into the polymer network produces no changes in the electronic properties of the polymeric material. However, Fig. 8 shows that when RH increases the total resistance value changes. Two well defined zones can be observed. In zone 1 (up to 65% of RH) the signal decreases at increasing RH. It indicates that the electrical resistance decreases because the pores, initially filled with dry air, are progressively filled with water which has a higher dielectric constant than air [36]. In this zone, the total resistance change can be attributed mainly to the change in R_{med} (Eq. (4)), taking into account the EEP results (Fig. 7) which show that, in the same RH range, there are neither changes in the electronic properties nor variation in the thickness of the polymer.

$$\Delta R_T = \Delta R_{med} \tag{4}$$

In zone 2, from 65 to 90% RH, the polymer film continues absorbing water but it starts swelling (see Fig. 7B), causing an increase in the separation of the polymer chains. This hinders the electron hopping process and increases the electrical resistance of the polymeric

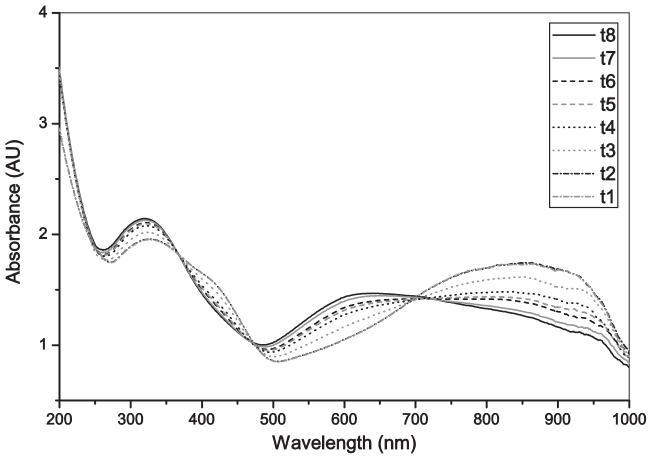

Fig. 5. UV–visible spectra of a PANI film at different times t (in seconds) while the PANI film changes from the insulator (in presence of ammonia vapor) to the conductive form (exposed chrlorhydric acid vapor).

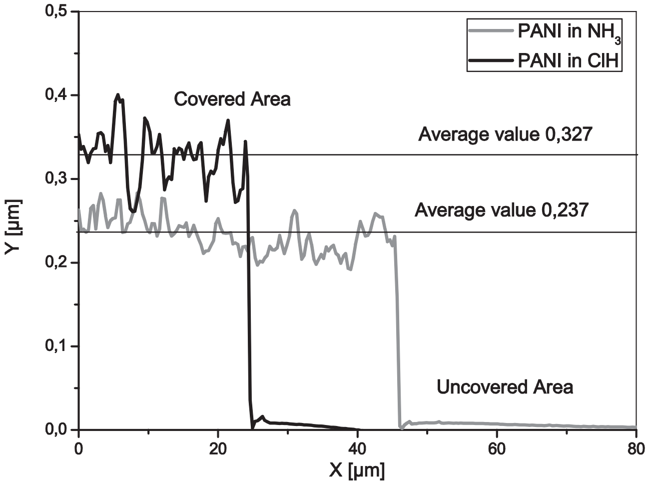

Fig. 6. Modifications in height of PANI film when it changes from the insulator to the conductive form.

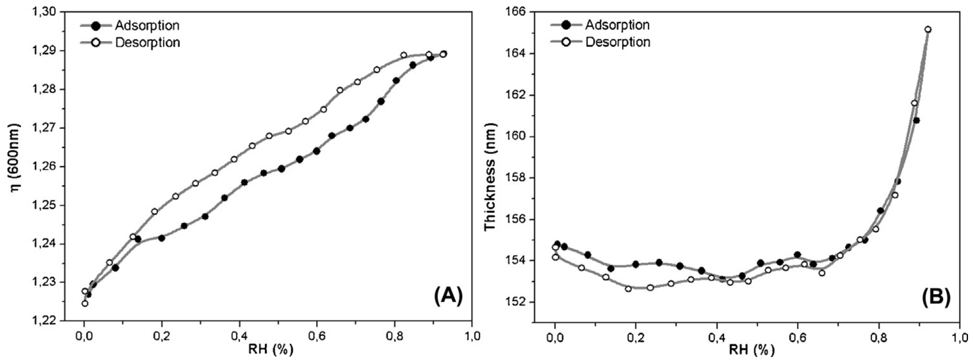

Fig. 7. Changes in (A) refractive index (n) and (B) thickness of PANI films vs RH during a water adsorption–desorption experiment.

material. The combination of the two effects (change of dielectric medium and swelling) (Eq. (5)) explains the smaller slope of the signal-humidity plot in this zone, in comparison with zone 1:

$$\Delta R_T = \Delta R_{med} - \Delta R_{hop} \tag{5}$$

The amount of analyte (water, alcohols, ketones or alkanes) absorbed by the polymer depends on the distribution constant for a given condition of temperature and vapor pressure, this is the equilibrium constant for the distribution of an analyte in both phases, solid and gas. The gas phase is a mixture of dry air and analyte vapor, whereas the solid phase is the polymer. Moreover, the gas phase composition in the headspace, the kind of analyte and the physicochemical properties of the polymer will also affect the process.

3.3. Effect of humidity on the sensor response

In the previous section we explained how the total resistance of the polymer can change when it interacts with pure analytes (water, alcohols, ketones or alkanes), with no other analyte interfering. In this section, we show how water vapor is an interference agent when using PANI films as organic vapors sensor.

Fig. 9 shows a typical PANI sensor response to butanol starting with the polymer stabilized at different initial RH values (0%, 20%, 40%, 60%, 80% and 100%). As it can be seen, depending on the initial RH value, the signal polarity can be positive, negative or nearly zero.

Fig. 9 shows the PANI film as a sensor of butanol. As can be seen, the films resistance decreases if the sensor is first stabilized for 20 min at humidity levels lower than 40%. Whereas if the film is first exposed for 20 min at humidity levels higher than 40%, the sensor resistance increases. This phenomenon is due to the difference between the distribution constants of water and butanol in the solid–gas system. The concentration of each analyte is also an important parameter because the distribution constant depends on the relative concentration of analytes.

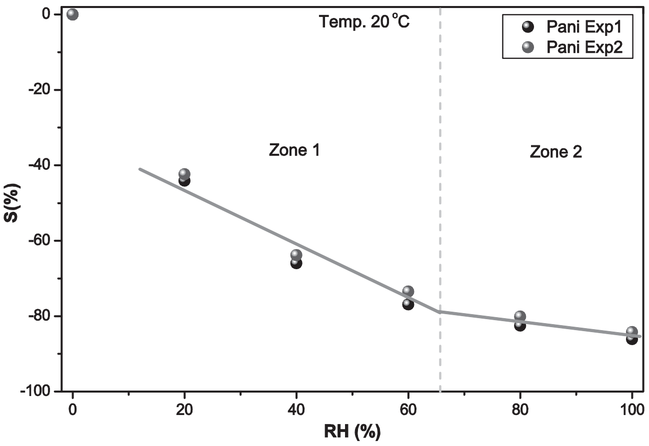

Fig. 8. Sensor signal (S (%)) vs RH values.

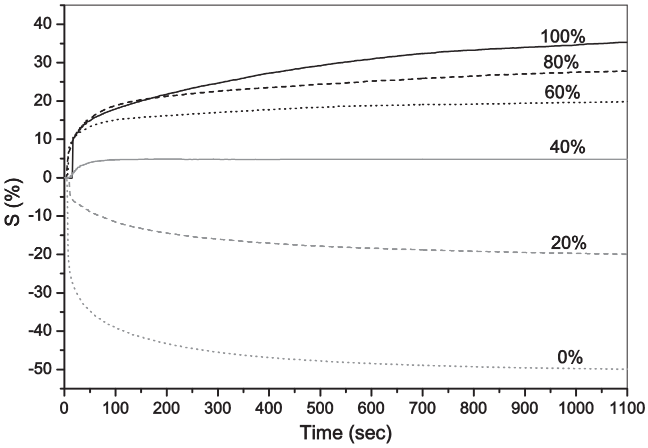

Fig. 9. PANI responses to butanol starting from different RH values at 20 °C.

Fig. 10 shows the dependence of the maximum response (the response value measured at long time e.g. 20 min) generated by the sensor to butanol and ethanol as a function of the initial RH. In this figure, we can found the exact value where the sensor response

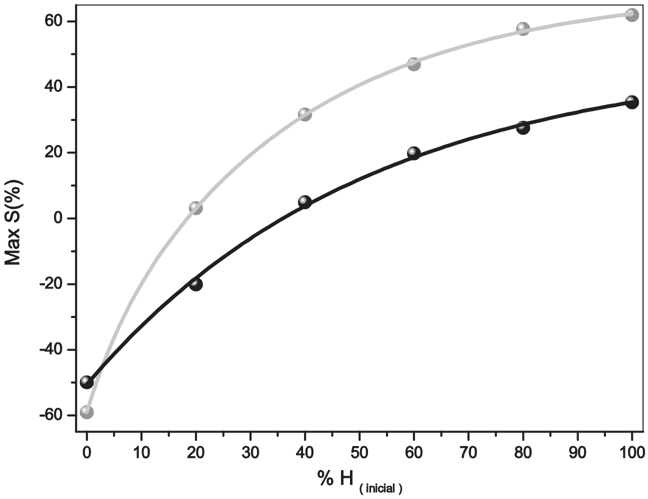

Fig. 10. Maximum response of the sensor to ethanol and butanol starting from different RH values at 20 °C.

changes polarity; the value for butanol under the mentioned conditions is 38% RH. For this RH value, when we try to sense butanol, the resistance of PANI film does not change.

For stabilization values lower than 38% RH, the amount of water molecules inside the polymeric material is small and the space intra-chains is nearly full of air. In this case, the absorption process of butanol molecules occurs without the release of water molecules contained inside its network. The ΔR_{med} must decrease because the butanol molecules enters into the polymeric network replacing the air and the dielectric constant changes from that of air (1) to a much higher value (18 for butanol). Therefore, the polymer film is more conductive.

When the sensor is stabilized at RH values above 38%, the signal is positive because the ΔR_{med} of the polymeric material increases when it is loaded with butanol vapor. In this range, the dielectric constant of medium decreases, because the water molecules initially contained inside the polymeric material is high and the butanol molecules have to expulse water molecules during the absorption process. Since the dielectric constant of butanol is significantly lower than water (80), the ΔR_{med} decreases and the conductivity of polymer film is lower.

During the absorption process, changes on R_{hop} are produced for all range of RH, but these changes are negligible in comparison with those changes on R_{med}.

Also, as can be seen in Fig. 10, the intensity of the signal ΔS (%) is highly dependent on the RH value. This phenomenon is very important because many authors use ΔS (%) or ΔR (Ω) to identify or quantify analytes using sensors based on PANI with no control of ambient humidity. This leads to non-reproducible measurements.

Fig. 10 also shows the dependence of the maximum response generated by the sensor to ethanol as a function of the initial RH. As shown before, the sensor produces a negative or positive response signal depending on the initial RH value. The RH value where the signal changes its sign is different for each particular analyte. For butanol, the signal changes from negative to positive sign at 38% RH while for ethanol the signal change occurs at 18% RH. This is because the distribution constant for ethanol is very different from butanol. Furthermore, the ethanol molecules displace the water molecules easily than butanol.

4. Conclusions

The resistance of PANI films is strongly affected by ambient humidity. Using two point resistivity and environmental ellipsometric porosimetry (EPP) it is found that, at low RH values, the water absorption only induces changes in the dielectric constant of the medium between the polymer chains. At high RH this effect is combined with a clear swelling of the film. Both EPP and UV–visible spectroscopy suggest that the changes on the intrinsic electronic properties of the polymer chains, due to humidity changes, are negligible. A similar absence of change in intrinsic electronic properties is observed when PANI films are exposed to different organic volatiles. This is contrast with the measured effect of acid or basic analytes, which changes the chemical doping of PANI chains. The mechanism proposed here can explain the changes in the resistivity when PANI is used as sensor for organics (alcohols, ketones, alkanes). It can also explain the bad reproducibility of this kind of polymeric sensor used without a strict ambient humidity control. The resistance changes of PANI films, upon exposure to volatile organic compounds (e.g. butanol), clearly depend on the RH values. Positive, negative or nearly zero changes can be obtained by adjusting the humidity. The signal (ΔS%) polarity depends on the distribution constant and the concentration of each analyte. Depending of conditions, the water molecules adsorbed on PANI film may be replaced by the analyte molecules. On one side, this means that a defined ambient humidity has to be set to use PANI films in volatile compounds sensors. Otherwise, no reproducible values are obtained. While dry air seems to be the best choice as carrier gas, the fact that adsorbed water replaces the adsorbed organic molecule gives an active mechanism to completely remove the adsorbed molecules and renewing the sensing surface. In that way, the sensor cleaning after measuring can be achieved using wet air.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.snb.2015.01.029.

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