

Diffusion of Organic Vapors in Materials for Gas Sensing Application

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Summary: Mass-variation measurements were carried out on carbon black (CB)-poly(vinyl chloride) (PVC) composite film with 40% by weight of di(2-ethylhexyl)-phthalate (DOP), cast on resonant piezo-layer (RPL) elements of lead zirconat titanate (PZT). Even if anomalous diffusion is predicted by fitting the data with $M_t/M_\infty = kt^\alpha$, the fractional uptake M_t/M_∞ is linear with the square root of the time up to $M_t/M_\infty = 0.6$, suggesting Fickian behaviour. The anomalous values of α are probably due to experimental time lag. A dependence of the diffusion on the morphology of the material and the penetrant shape and flexibility has been found.

Keywords: microbalance sensors; organic vapour sorption and diffusion; PVC composite films

Introduction

Carbon Black (CB)-Poly(vinyl chloride) (PVC) composite films with the addition of different concentration of plasticizers have been employed previously to prepare conductive sensors to be used in the gas sensing field [1]. All sensors were tested upon exposure to different organic vapors and the resistance responses were measured as a function of time or analyte concentration. From a qualitative point of view, it was found that the response rates were effected by the content of plasticizer. As expected they increased with the increase of plasticizer content in all the tested sensors. These results are consistent with the T_g values of the corresponding films because it is well known that the diffusion processes occur rapidly above the T_g [2]. We had also pointed out that the amount of organic vapour adsorbed at the equilibrium, decreases increasing the plasticizer concentration.

Starting from these results and considering that for practical application the most important design criteria for such systems is that they should rapidly transduce environmental information into an easily monitored signal, we have focused our attention on the response rate and on the diffusion process related to it.

Since among the CB-PVC composite films studied, the one with 40% by weight of DOP (PVC-DOP40) was the only well above its transition temperature ($T_g = -20.1^\circ\text{C}$) at room temperature, we have cast it on a 7MHz resonant piezo-layer (RPL) microbalance sensors and we have carried out mass-variation measurements with three different organic vapors.

As shown by Sauerebrey [3], changes in frequency are simply related to the mass accumulated on the resonant element:

$$\Delta f \propto K \Delta m \quad (1)$$

In this preliminary work, we have chosen a simple diffusion model to evaluate the nature of diffusion process. The most commonly used method is to fit the initial portion of the sorption curve with the empirical relation [4]:

$$\frac{Mt}{M_\infty} = kt^\alpha \quad (2)$$

where M_t is the mass of organic vapor absorbed at time t and M_∞ that at complete equilibrium; k is a parameter that depends on the structural characteristics of the material in addition to its interaction with penetrant molecules. The value of α is indicative of the type of the transport mechanism.

For a slab geometry, anomalous diffusion is indicated by $0.5 < \alpha < 1$, while $\alpha = 0.5$ corresponds to Fickian diffusion. Many factors may produce anomalous features: non planar geometry, time-dependent surface concentration, anisotropic dimensional changes in the polymer sample and polymer relaxation, even if the rate-controlling process is Fickian at the molecular level [5].

The purpose of this work is to evaluate the nature of the diffusion and to highlight how the morphology complexity of our systems effects the transport process.

Experimental Section

Materials

Carbon black (Printex XE2B) was a kind gift from Degussa-Hüls Chimica S.p.A.. PVC ($\overline{M}_w = 95000$), DOP was purchased from Aldrich Co. Acetone, hexane, ethanol and

tetrahydrofuran (THF) were reagent grade solvents from Aldrich Co. All materials were used as received.

Instruments

The measurements of film vapor sorption were carried out by means of a dedicated system based on arrays of variable-mass, i.e. microbalance sensors, which were resonant (7MHz) piezo-layer (RPL) elements of lead zirconate titanate (PZT) screen-printed on alumina substrate, as previously described [6]. The system comprised a stainless-steel sensor test chamber, the conducts and electronic mass-flow regulators for controlled vapor introduction in the test chamber, and an electronic board containing the sensor oscillators and the circuitry to interface with a personal computer, which supervised the whole system.

Scanning Electron Microscopy (SEM) investigations were performed with a Cambridge S260 microscope on gold sputtered sensors.

Preparation of the Sensors

Composite films were obtained by spray from a suspension prepared as follows: 80 mg of organic matrix (PVC and 40% by weight of DOP) were dissolved in 10 ml of THF and 20 mg of carbon black were added. The mixture was sonicated for 5 minutes and it was diluted with 10 ml of THF, therefore it was sprayed on one RPL element until obtaining a frequency shift of about 20kHz. The films were finally dried in air for 24 hours before use. The same procedure was followed to prepare films without carbon black.

Frequency Measurements

The frequency shift versus time was measured simultaneously for three sensors, one for each amount of CB in the film plus an uncoated RPL element (blank). We took the measurements by keeping a gas flow in the sensor chamber constant at 500 ml/min. Up to time t_1 , the flow was made entirely by nitrogen; at time t_1 the electronic mass-regulator split the nitrogen flow into two streams: one remains dry and the other was saturated in a gas/liquid contacting vessel. Then, before entering in the sensing chamber, the dry and the saturated streams were recombined. At time t_2 , the electronic mass-regulator stop to split the nitrogen flow and only a dry stream was introduced in the chamber. All the measurements were carried out at 22°C.

Results and Discussion

Morphological Characterisation of the Sensors

In Figure 1 are reported the micrographs of the filled and unfilled sensors and, for comparison, that of the piezo-layer element uncoated. In the first place, we have to point the attention on the porosity of our supports (Fig.1 (a)). This is a good starting condition in term of increasing the contact area of the sensing films, but means an approximation in terms of diffusion study, which require a flat surface.

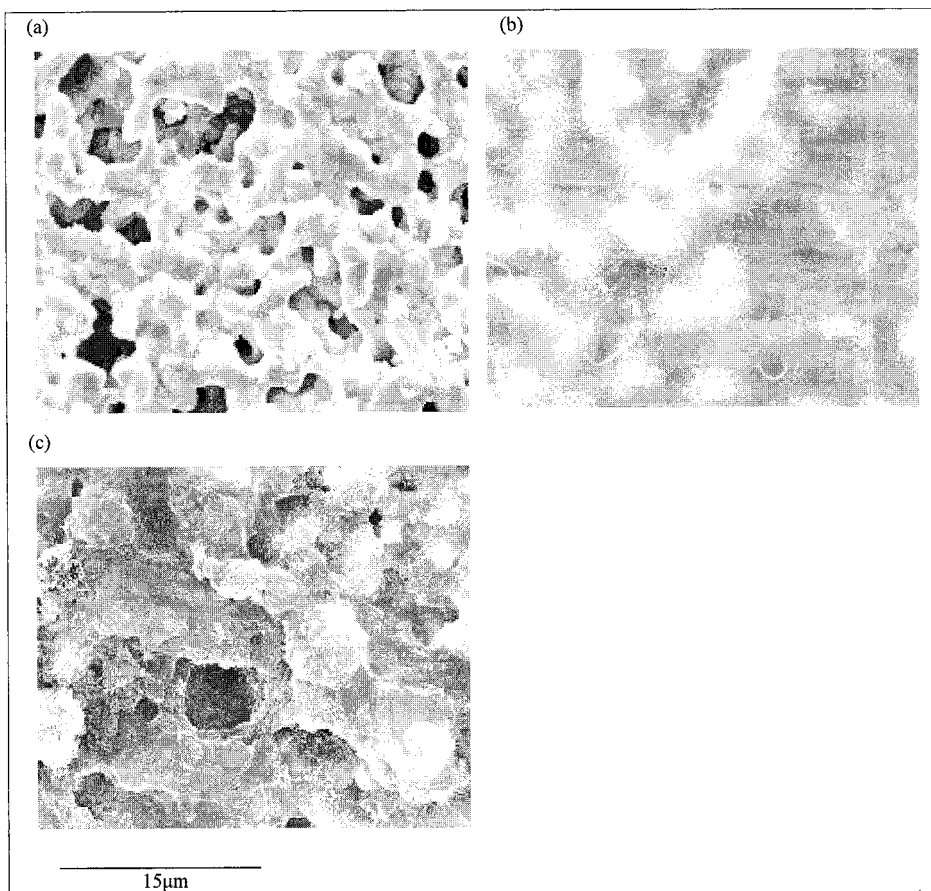


Figure 1. SEM micrographs of the studied sensors: (a) blank, (b) PVC-DOP40 and (c) the PVC-DOP40 with 20% of carbon back.

In the same direction acts the addition of carbon-black, as it is shown in Figure 1 (c). In the second place, but it is not of minor importance, we can say that our deposition method is able to give a continuous film (see Figure 1 (b)).

The Nature of the Diffusion

Figure 2 displays the conductometric and the gravimetric response of PVC-DOP40 sensor with 20% by weight of CB upon exposure to 32 ppth of acetone. It is interesting to note that, after a contact time of 3 minutes, all the resistance change appends for a mass gain of 60%. This suggests to consider the sorption only up to $M_t/M_\infty=0.6$ just because this is the portion of the curve related to the electrical response of the sensor.

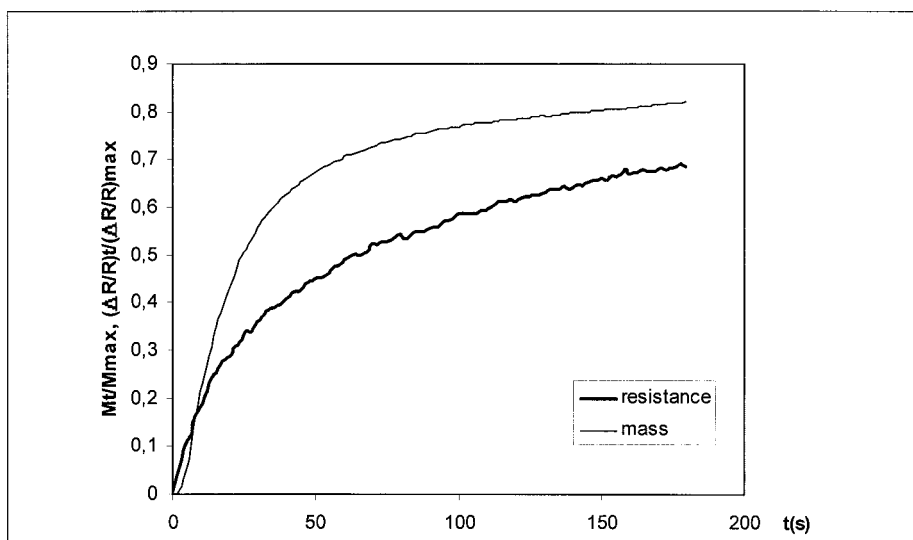


Figure 2. Conductometric and gravimetric response of the PVC-DOP40 composite, filled with 20% by weight of CB. The sensors were exposed to 32 ppth of acetone for a contact time of three minutes. The measurements were carried out simultaneously and at 22°C.

To understand the nature of the diffusion in our composites, we fit the exponent α in Eq.(2) to our experimental data. Table 1 summarizes the results.

Table 1. Exponent α and K parameter in Eq.(2) for the organic vapors tested.

| | PVC-DOP40 0% CB | | | | PVC-DOP40 20%CB | | |
|----------------|-------------------|-------------------|----------|------------------|-------------------|----------|----------------|
| | ppth ^a | K·10 ² | α | R ^{2,b} | K·10 ² | α | R ² |
| Hexane | 30 | 3.22 | 0.99 | 0.993 | 3.42 | 1.00 | 0.993 |
| Ethanol | 13 | 2.70 | 1.03 | 0.992 | 3.31 | 0.90 | 0.980 |
| Acetone | 32 | 2.14 | 0.91 | 0.980 | 2.93 | 0.89 | 0.974 |

^a Organic vapor concentration in the recombined stream flow.^b R² is the square of the correlation coefficient.

For both sensors and all organic vapors tested, the values of α purpose an anomalous diffusion. Moreover, the values of K decrease from hexane to acetone for both type of sensor suggesting a decreasing in film-vapor interaction. On the other hand, the morphological modification caused by the introduction of carbon black seams to improve the composite-vapor interaction. In fact, the values of K of the filled films are higher than of the unfilled.

If we plot M_t/M_∞ versus $t^{0.5}$, better linear correlations ($R^2 \geq 0.993$) are found; however, the linear fits produce a non zero intercept with the time axis, as reported in Table 2. This suggests that after a short time lag, the diffusion processes follow Fickian kinetics. The time lag in our data probably follows from an unavoidable experimental artefact: it is not possible to raise instantaneously the organic vapor surface concentration to the equilibrium value. We carry out the measurements by keeping the nitrogen flow in the sensing chamber constant at 500 ml/min and we collect the data starting from the instant when the electronic mass-regulator splits the nitrogen flow into two streams. One streams remains dry and the other is saturated in a gas/liquid contacting vessel. Then, before entering in the sensing chamber, the dry and the saturated streams are recombined. Therefore, the time lag may be a source of an anomalous α , arising from a delay in raising the penetrant surface concentration to the equilibrium value.

The diffusivity (D) can be determined from the following equation [7]:

$$D = \frac{\pi}{16} \delta^2 K^2 \quad (3)$$

where δ is the film thickness and K is the slope of the reduced sorption curve (M_t/M_∞ plotted versus $t^{0.5}$). The calculated diffusion coefficients are listed in Table 2.

Table 2. Intercepts and correlation coefficients of the reduced sorption curves and the corresponding diffusion coefficients (D) calculated with Eq.(2).

| | PVC-DOP40 0% CB | | | PVC-DOP40 20%CB | | |
|----------------|-----------------|------------------|-----------------------|-----------------|------------------|-----------------------|
| | A ^a | R ^{2,c} | D(cm ² /s) | A ^a | R ^{2,c} | D(cm ² /s) |
| Hexane | -0.424 | 0.998 | $1.80 \cdot 10^{-8}$ | -0.468 | 0.998 | $2.19 \cdot 10^{-8}$ |
| Ethanol | -0.362 | 0.997 | $1.47 \cdot 10^{-8}$ | -0.463 | 0.993 | $1.51 \cdot 10^{-8}$ |
| Acetone | -0.176 | 0.995 | $0.44 \cdot 10^{-8}$ | -0.271 | 0.993 | $0.80 \cdot 10^{-8}$ |

^a R² is the square of the correlation coefficient.

^b A is the intercept.

^c The average thickness of the films is 13 μm.

First of all, we can say that the effect of the conductive filler on the diffusivity can be considered irrelevant for ethanol sorption, being the diffusion coefficients of the filled and the unfilled sensor respectively $1.51 \cdot 10^{-8} \text{ cm}^2/\text{s}$ and $1.47 \cdot 10^{-8} \text{ cm}^2/\text{s}$. On the other hand, the addition of carbon black seems to have some relevance for hexane, increasing the diffusion coefficient from $1.80 \cdot 10^{-8} \text{ cm}^2/\text{s}$ to $2.19 \cdot 10^{-8} \text{ cm}^2/\text{s}$, while the strongest effect is observed in the case of acetone sorption, going from $0.44 \cdot 10^{-8} \text{ cm}^2/\text{s}$ to $0.80 \cdot 10^{-8} \text{ cm}^2/\text{s}$.

Secondly D decreases from hexane to acetone for each type of sensors, showing the same trend of the corresponding K parameters discussed above. These results are consistent with what is known from literature [8]. The molecular size and shape of a penetrant significantly influence its diffusivity in the material. The smaller but more rigid diffusing molecules (e.g., acetone, ethanol), have a lower diffusion coefficient than a larger but more flexible one (e.g., hexane). This is attributed to molecular shape, which modifies the effect of molecular size.

Conclusions

Mass sorption of organic vapors in composite films, previously used as conductive sensors, have been studied by the use of piezo-layer elements of lead zirconate titanate.

In spite of the morphological complexity of the systems, a simple empirical equation can describe quite well the transport processes inside the studied materials, suggesting anomalous diffusion. Nevertheless, the same equation written for Fickian behaviour fits better our data. At this moment, these results can not be considered in contrast, because a plausible reason of anomalous values of α is the experimental time lag. However, more research is necessary.

The diffusion coefficient of this study have shown a dependence on the morphology of the material and the penetrant shape and flexibility.

- [1] M.Penco, L.Sartore, F.Bignotti, S.Della Sciucca, F.Ferrari., P.Crescini, S.D'Antone, J.Appl.Polym. Sci **2004**, 91, 1816.
- [2] J.Crank, G.S.Park Diffusion in Polymers **1968**, Academic: London.
- [3] G.Z.Sauerbrey Physics **1959**, 155, 206.
- [4] T.M.Aminabhavi, H.T.S.Phayde Polymer **1995**, 36, 1023.
- [5] S.H.Gehrke, D. Biren, J.J.Hopkins J. Biomat., Sci.-Polym. Ed.**1994**, 6, 375.
- [6] V.Ferrari, D.Marioli, A.Taroni Sens.and Actuators A **2001**, 92, 182.
- [7] D.W.Van Krevelen Properties of Polymers **1976** Elsevier Scientific Publishing Company.
- [8] M.Saleem, A.F.A.Asfour, D.De Kee J.Appl. Polym. Sci. **1989**, 37, 617.