Smart Poly(styrene)/Carbon Black Conductive Polymer Composites Films for Styrene Vapour Sensing

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Summary: Conductive Polymer Composites (CPC) can be used to elaborate sensing elements able to detect solvent vapours at very low concentrations (some ppm). Our experiments have shown that combining atactic PS or syndiotactic PS to five carbon black of different specific surfaces, allows obtaining a wide range of electrical resistances and surface morphologies. The CPC films have been elaborated from solutions by spraying and spin coating, the former being more adequate to design sensitive films with tuneable electrical properties. The larger electrical responses were obtained with an initial resistance close to 10^4 Ω. Our sensors gave a response for very low styrene concentration (some ppm) increasing as a function of vapour concentration.

Keywords: carbon black; conductive polymer composites; poly(styrene); vapour sensing

Introduction

Polymer films are often used in sensors design [1-3]. But in particular, associating an insulating polymer matrix to a conductive filler which provides electrically conductive polymer composites (CPC) leads to materials with very interesting sensing properties. In fact, the important resistivity variation of CPC with thermal [4], mechanical [5] or chemical [6-10] solicitations make possible their use as transducers. For vapour sensing, expected characteristics are: large electrical response, short response time, high sensitivity and important vapour selectivity. The first point is related to the CPC initial resistivity, the second to the CPC thickness, the third to the CPC specific surface and the later to the interactions between solvent vapour molecules and CPC matrix macromolecules. The design of low cost sensors able to detect volatile organic compound (VOC) such as methanol, toluene, chloroform and styrene used in composites processing or chemistry industries is of interest with regard to the new environment standards being applied in Europe.

In this study we have investigated the influence of several parameters as the CPC deposition process, the initial resistivity and the vapour concentration, on some poly(styrene)/carbon black (PS/CB) sensors electrical response to styrene vapours.

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Experimental

Materials: Five carbon blacks (CB) of different specific surface areas (cf. **Table 1**) have been dispersed in two poly(styrene) (PS) matrices atactic and syndiotactic (cf. **Table 2**) in solution. Toluene, o-dichlorobenzene and styrene were provided by ACCROS.

Table 1. Polymers characteristics.

	sPS	aPS
T_g (°C)	98	105
T_m(°C)	270	-
$T_{c,n}$(°C)	242	-
M_n (g.mol^{-1})	94 100	2 500
M_w (g.mol^{-1})	192 000	-
Tacticity index (%)	0.99	-
$\Delta H_m/\Delta H_\infty$ (J.g^{-1})/ (J.g^{-1})	53.2/98	-
Density (g.cm^{-3})	1.05	1.05
Supplier	Resinex- Dow	PolySciences

Table 2. Carbon blacks characteristics.

Supplier	Degussa	Degussa	Erachem	Erachem	Erachem
Type	Corax N550	N115Corax	Ensaco150G	Ensaco250G	Ensaco350G
BET N_2 ($m^2.g^{-1}$)	44	143	50	65	770
CTAB ($m^2.g^{-1}$)	42	128	-	-	-
DBP ($cm^3.100g^{-1}$)	121	113	165	190	320
Diameter (nm)	40	29	40	38	35

Sample preparation: aPS flakes were first introduced in the reactor and then dissolved in toluene under stirring at 100°C for 1 hour to obtain solutions at 20 g.dm^{-3}. sPS pellets, less soluble due to their high melting temperature (T_m) and crystallinity (X%) were dissolved in o-dichlorobenzene at 150°C for 2 hours at a lower content 5.5 g.dm^{-3} to prevent gel formation. In a second step, carbon black was introduced in the reactor under sonication for 1 hour to obtain homogeneous solutions with a CB/PS weight ratio of about 12/100.

Sensor processing: Two deposition processes where used, spraying and spin coating. For the first process an air pressure of 0.2 MPa was applied for 1.30 s at respectively 100°C and 150°C for aPS and sPS for each layer deposition whereas for the second process, drops of 10^{-3} cm^3 were deposited under rotation (index 2) during 10 s. The sensor substrate consisted in interdigitated copper electrodes engraved in a typical epoxy board (cf. **Figure 1**). After spraying, the surface of the substrate is coated with a homogeneous CPC film (cf. **Figure 2**).

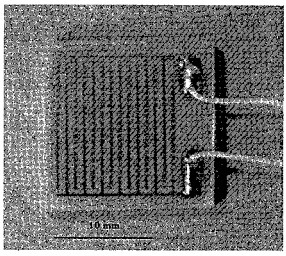

Figure 1. Interdigitted electrodes before CPC deposition.

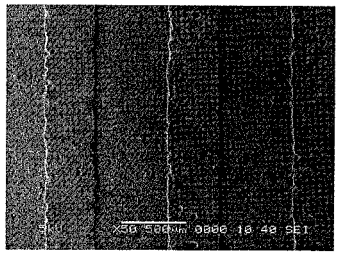

Figure 2. SEM picture of the CPC sensor.

Characterization: *Electrical resistivity* was derived from the intensity and voltage measurement with a KEITHLEY 2000 multimeter. Tension was adjusted with a stabilized source. Considering the important resistance of the samples, a two-probe technique was used. Collection and processing of data was done by an acquisition program developed with VISUAL DESIGNER 4.0 described in a previous work [9]. *Calorimetric measurements* were made on a PERKIN ELMER PYRIS 1 differential scanning calorimeter (D.S.C.). The calibration was done with indium and zinc. The base line was checked every day. Aluminium pans with holes were used and the samples mass was approximately 10 mg. All the temperatures measured from a peak extremum ($T_{c,n}$, T_m) are determined at less than ± 0.5°C and from a sigmoid (T_g) at less than ± 1°C. *Morphologies observations* were done with a JEOL JSM-6031 scanning electron microscope (S.E.M.).

Results and Discussion

The processing of the active CPC film is a very important step which determines many of the sensors characteristics. We have seen in a previous work [10] that the thinner the active film was the shorter the response time, so that in this study we have used two techniques known to allow obtaining thin film, spraying and spin coating. Once the deposition conditions have been optimised, pressure, speed, time, solution temperature and solutions concentration were maintained constant and only the nature of the solution, i.-e., the PS and CB was changed.

Influence of the deposition technique on electrical properties of the CPC active film: For both processes, conductivity of the samples is achieved through the percolation of CB particles resulting from the layers superposition. **Figure 3** & **Figure 4** show that the initial resistance of the sensor can be adjusted by the number of layers sprayed and also by the nature of poly(styrene) and carbon black. For sPS-CB the increase in conductivity of the

sample is well correlated to an increase in specific surface of carbon black (cf. **Table 2**), but for aPS CPC, 250G gives a higher conductivity than expected from the carbon black characteristics. To explain the differences of electrical behaviour between aPS and sPS, it must be recalled that their thermo-physical characteristics are very different (cf. **Table 1**). sPS is less soluble due to its high crystallinity and melting temperature, and thus the concentration of the solution used for deposition is ten times lower than that used with aPS. More, the structuring of conductive pathways during sPS crystallisation tend to concentrate carbon black in the amorphous phases and increase conductivity compared with aPS at the same CB content. Thus it not surprising to obtain CPC films of aPS and sPS matrix with comparable resistance although shifted of about one resistance decade.

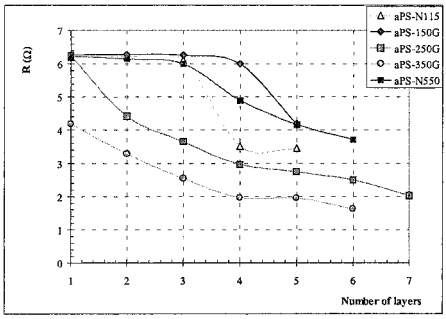

Figure 3. Resistivity decrease with the number of CPC layers for different aPS/CB associations by spraying.

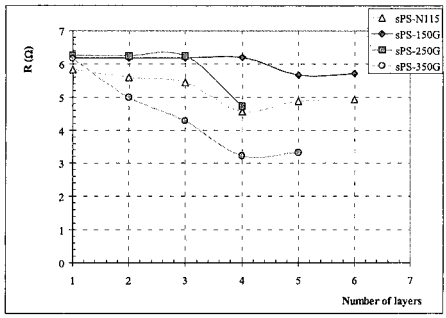

Figure 4. Resistivity decrease with the number of CPC layers for different sPS/CB associations by spraying.

Using spin coating (**Figure 5** & **Figure 6**) also allows obtaining samples with tailored resistance. The resistances of aPS CPC films are comparable to that obtained with spraying (excepted for N115 less conductive), but the resistance of sPS CPC films is much more important even with the more conductive CB (350G). More, the surface morphology shows clearly that the CB particles, denser than the polymer phase, are more sensitive to centrifugation and form large branches from the centre, clearly visible to the naked eye, which are harmful to the conducting network homogeneity. This is the reason why spraying was preferred to spin coating for the elaboration of the thin CPC active film.

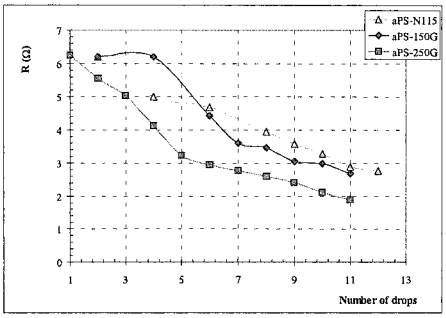

Figure 5. Resistivity decrease with the number of CPC drops for different aPS/CB associations by spin coating.

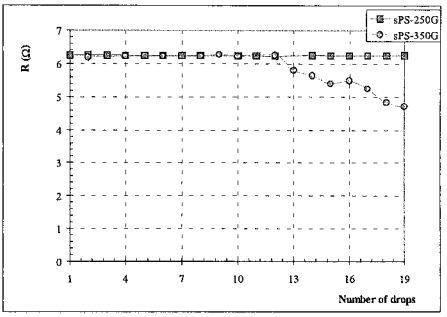

Figure 6. Resistivity decrease with the number of CPC drops for different sPS/CB associations by spin coating.

Morphology of CPC active film: The morphologies of the films obtained by spraying and for different combinations of PS and CB are presented in **Figure 7** to **Figure 14**, on the left side for aPS CPC and on the right for sPS. The comparison of **Figure 7** & **Figure 8**, **Figure 9** & **Figure 10** and **Figure 11** & **Figure 12**, respectively show that the surface morphology depends mainly on CB characteristics whereas the PS nature and the numbers of layers seem to be less important. Nevertheless, the morphology at this scale, and the related specific surface, is certainly less decisive for solvent diffusion and sensing than it is at higher magnification as illustrated by the comparison of **Figure 12** & **Figure 14**. In this later, aggregates of several thousands nanometres are clearly visible at the surface of micro pores. In fact, it is the perturbation due to solvent molecules diffusion in of such aggregates, provided that they are interconnected, that generates an electrical signal adequate for sensing.

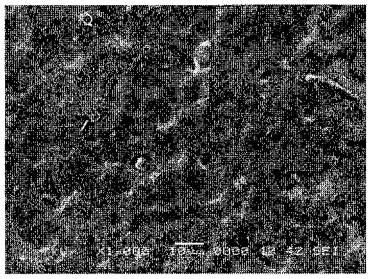

Figure 7. S.E.M. picture of aPS-N115, 2 layers.

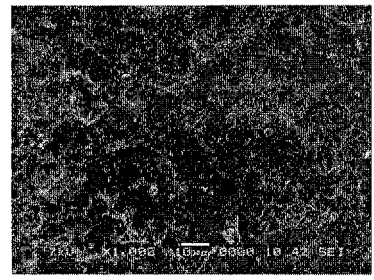

Figure 8. S.E.M. picture of sPS-150G, 5 layers.

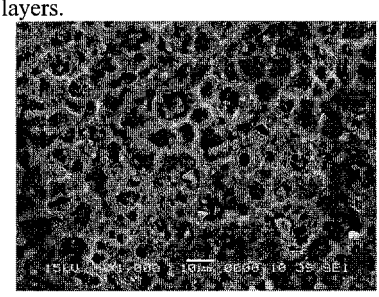

Figure 9. S.E.M. picture of aPS-250G 3 layers.

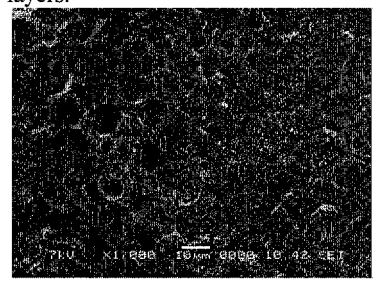

Figure 10. S.E.M. picture of sPS-250G, 3 layers.

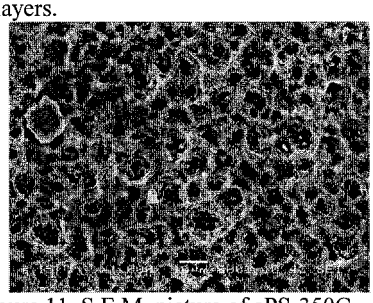

Figure 11. S.E.M. picture of aPS-350G 2 layers.

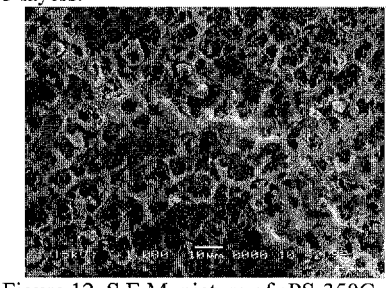

Figure 12. S.E.M. picture of sPS-350G, 3 layers.

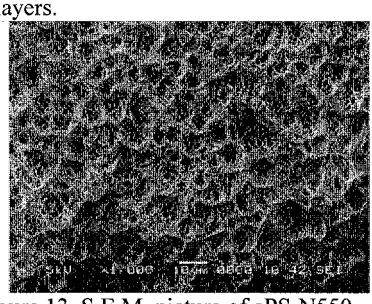

Figure 13. S.E.M. picture of aPS-N550, 5 layers.

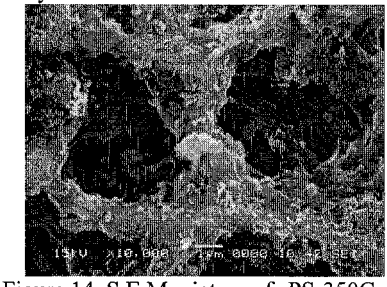

Figure 14. S.E.M. picture of sPS-350G, 3 layers.

Responses of the sensors to styrene vapours: Once the influence of the processing conditions and resulting morphologies on the sensing film electrical properties have been stated, it is finely interesting to study the impact they have on styrene vapour sensing. The response to a defined vapour can be defined by the ratio of the resistance amplitude to the initial resistance. Figure 15 shows that in the presence of 3 ppm of styrene vapour, increasing the initial resistance R_0, also increases the electrical response $\Delta R/R_0$. It is thus important to adjust R_0 during the elaboration and processing steps for each system to optimise the sensing. Another important point is to check that the electrical response is proportional to the vapour concentration. Figure 16 shows that the first results obtained for aPS-N115 in two different styrene atmospheres are promising, as even at very low vapour concentration (some ppm) the sensor is able to give a more important response at more important vapour concentration. Additional work is now in process to confirm that the responses obtained with our PS-CB sensors are quantitative for all the system studied, in a wide range of concentration and for different vapours.

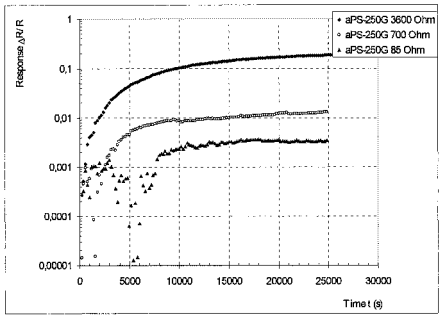

Figure 15. Responses of aPS/CB sensors to 3 ppm of styrene for different R_0 (85, 700, 3600 Ω).

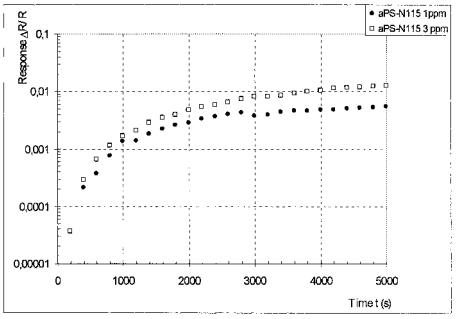

Figure 16. Responses of aPS/N115 (R_0 = 2700 Ω) sensors to 2 styrene concentrations (1, 3 ppm).

Conclusion

Different CPC films used for vapour sensing have been elaborated from solutions by spraying and spin coating. The former process appears to be the more reproducible and adequate to design sensitive films with tuneable electrical properties. Our experiments have shown that combining aPS or sPS to five kinds of carbon black allows scanning a wide range of electrical resistance and surface morphologies to elaborate smart films for vapour sensing. For our systems an initial resistance close to 10^4 Ω appeared to give an optimal response. In these

adequate conditions of elaboration and processing, our sensors gave a response for very low solvent concentration (some ppm) increasing as function of vapour concentration. Future works will concern the selectivity of these sensors to different vapours.

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