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Thickness effect on the solvent sensing parameters of carbon black-polymer composites

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Abstract

Study of the sensing parameters: sensibility, response and recuperation times to hexane vapors for layers of different thickness of poly(butadiene) + carbon black (CB) composites is presented. The results show that sensibility increases as the CB- weight percent diminishes, being in agreement with reported results by several researches. In this work another variable was studied on the sensing parameters, the thickness. The initial electrical resistance of the studied layers increases until three magnitude orders as diminish theirs thickness and the sensibility in this study increases until one magnitude order as the layer thickness diminishes around 0.25 μm.

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1. Introduction

One of the practical applications of CPs is their use as sensors [1], where the detection mechanism is well explained by the concepts of percolation. In these materials the electric conductivity can be modified varying the

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PM volume during a sensing experiment, producing a disconnection-reconnection of the electric paths. That is why at concentrations close to the percolation threshold [1] it can be observed a higher detection sensitivity of the vapor. However around the threshold, the reproducibility of the electrical properties of the CPs is very low and the standard deviation of the resistivity values is greater than 100% [2]. This is reasonable since in the percolation threshold there is a minimum amount of particles forming conductive paths and any variation in the preparation of the compound will result in a different arrangement of such paths. As a consequence of this, a significant variation of the CPs electrical properties will be observed [2]. At higher CB concentrations than the percolation threshold reproducibility of the electrical properties is very reliable and additionally the current voltage relationship is linear which facilitates the resistance measurement. However, in this composition range the CPs sensitivity decreases due to a minor portion of polymer exposed to the interaction with the vapor compared to that exposed in CPs compositions close to the percolation threshold. Thus the CB composition in the CPs is a key factor to control the sensitivity. Also the sensing parameters of a particular composite are controlled by: the mechanisms of the solvent diffusion into the composite, the carbon black distribution into the composite, the temperature and by the used method for sensing test, mainly [3 -7].

Recently it has been proposed that the sample thickness [7] is critical for sensing applications of polyvinylpyrrolidone and CB composites. This is because in the CPs an additional variable that allows monitoring of the electrical properties is their thickness [8,9], Fig.1(a). This paper proposes to use composite layers at concentrations greater than the percolation threshold.

On the other hand there is the advantage that at high CB concentrations, there is a good control of the electrical properties and by thickness control we can improve sensing ability: sensitivity and consequently reproducibility with an ease measurement; also the observed response times are the only of a few seconds.

Nomenclature

CB	Carbon Black XC72, Cabot.
THF	Tetrahydrofuran
PBD	4-*cis* Polybutadiene
CPs	Carbon black-polymer composites
PM	Polymer Matrix
DC	Direct Current
mℓ	Millilitres
s	Seconds
h	Hours
l	Litres
min	Minutes
%wt	Weight percent

2. Experimental

2.1 Materials

The used materials in this work were PBD and THF from Aldrich, CB donated by Cabot. Coop., Corning slides glass substrates and SPI Silver paint, 70% solids, Electron Microscopy. Oil-free air dried using different filters including a refrigeration dryer Garner Denver. All these were used without any pre-treatment.

2.2 Polymer matrix and composite layers preparation

The CPs were prepared by solution method according to the methodology previously developed in other studies [8-12]. The composite layers were deposited by spin coating and their thickness was controlled by successive deposits of the composite solution, as reported previously [8,11,12]. The layer thickness was measured with a profilometer, Sloan Dektak IIA.

2.3 Sensing experiments

For detection experiments of Hexane a sensing chamber implemented in our laboratory was used. In this system the film sample was exposed to an air flow free of moisture and oil, which after was "contaminated" with the solvent applied with a syringe. With this arrangement, we defined two types of experiments [12]: 1) Progressive Sensing and 2) Multiple Sensing at Constant Volume. The first consisted in to expose the layer samples to a progressive increment of the solvent. Solvent pulses were applied from 0.1 to 1 *ml* with increments of 0.1 *ml*. After completion of all the pulses, the sample was dried into a vacuum desiccator for 24 h and again it was exposed to the same process until deterioration of the sample. For the case of Multiple Sensing, samples were subjected to repetitive pulses of the same amount of hexane (0.5 *ml*) until deterioration of the sample. In both experiments the air flow was constant at *1l/ min*. An example of this experiment is shown in Fig.1 (b). With those results, sensing parameter as the sensitivity, response and recovery times, and also the sensing cycles before deterioration were obtained.

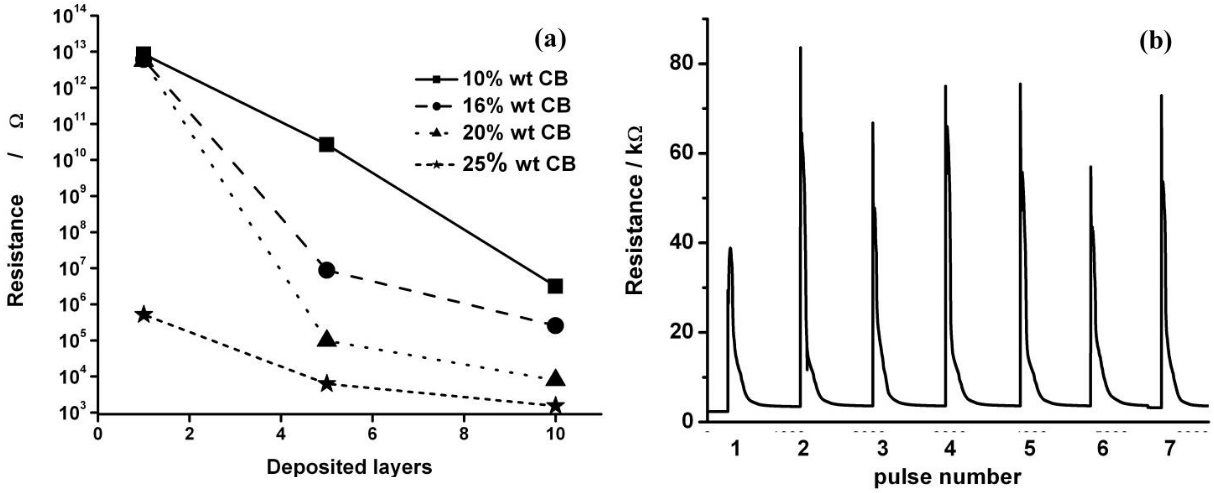

Fig. 1. (a) Resistance of CPs layers as a function of composition and of deposited layers; (b) Multiple hexane sensing with a 20%wt CB CPs for 0.5*ml* of hexane

2. Results

We report the sensing parameters results for two different layer thicknesses and two CB concentrations (20 and 25 % wt) evaluated in CPs based on a PBD matrix, Table1.

Table 1. Sensing parameters for layers of PB + CB CPs obtained by sensing 0.5*ml* of hexane, in a multiple sensing experiment.

% wt CB	Thickness (μm)		Sensitivity ($\Delta R/R_0$)		Response time (s)		Recovery time (s)	
	5 layers	10 layers	5 layers	10 layers	5 layers	10 layers	5 layers	10 layers
20	0.363	0.637	19	0.3	2	13	160	108
25	0.583	0.788	0.2	0.03	1	3	96	161

According to expectations is clear that the sensitivity can be controlled by both: the thickness and the CB concentration. A higher CB concentration it could be appreciated a decreasing in sensitivity, regardless of the thickness, which agrees very well with the results in the literature. But from the point of view of the thickness, is evident that the sensitivity increases as the thickness decreases, independently of the CP´s composition. A reduction in thickness of about 50% provides one order of magnitude higher in sensitivity, being the highest in this study for the thinnest film of the 20 %wt CB composite. This effect can be explained by a phenomenological model which consists in considering the polymer composite exposed to the solvent, as a system of two electrical contributions connected in parallel. In this way the thickness decrement of the layer over the individual contributions would be significant. This model will be described in detail in the large contribution.

Three samples of 20 %wt CB could be submitted to 6 cycles of sensing before they detriment. It is noteworthy that the statistic error was about 23% .

The time resolution in which the data sensing were recorded was 1 second. It is to be noted that in terms of the amount of solvent pulses, both response times as relaxation do not show a decreasing or increasing tendency with respect to this amount. Values of average response time are presented in Table 1. The response time of around 3 seconds were observed in layers of 25 wt% CB, independently of the thickness. However, for samples at 20 %wt CB is obvious that the thickness plays an important role. The response time is 2s for sample of 5 layers whereas samples of 10 layers showed a response time of 13s. Note that detection times achieved from these experiments are much lower than those reported in the literature. For example, [13] reported a response time from 150 to 400 s in WPU/ CB and 3.5 %wt CB composites exposed to 10 parts per trillion of acetone. Their recovery times were between 50 and 100 s.

The recovery times for all evaluated samples were in the range of 100-150s without observing a clear tendency respect to the amount of CB and to the thickness. In some sensing publication as the mentioned before have reported recovery times in the same range.

Finally we can conclude that is possible improve the sensing ability with the thickness of a layer polymer composite: Thinner thickness improves the sensitivity. There are some goals we have to achieve for sensing evaluations such as the improvement of the deposition technique in order to control the thickness of the layers, to implement an automatized injection process of the solvents, measurements of solvent volumes in the range of milliliters and to prove the described model for composites constituted of other polymer matrixes.

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