Fabrication and Characterization of Sensitive Polymer (Nano)Composites

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Summary: We report on the fabrication process of a polymer sensing device based on a thin film composite obtained by spinning or casting a carbon fillers/thermoplastic polymer dispersion on a glass substrates. In this work we produce thin composite films characterized by different grade of dispersion of carbon black in polymer matrix (Poly(methyl-methacrylate), Poly(2 hydroxy-ethyl-methacrylate) and atactic poly(styrene)). We discuss, in particular the effect of the polymer and filler characteristics on the thin film morphology. Device material response towards different analytes will be also discussed. Size distribution of filler in polymer suspension and deposition method type strongly influence homogeneity and conductivity of corresponding polymer composite films and finally their sensor properties.

Keywords: carbon black; composites; nanotubes; sensor; volatile organic compounds

Introduction

Polymers applications as sensitive materials have attracted a great scientific and commercial interest during the last few years. Conducting polymeric materials can be obtained in two ways: by producing a polymer that is intrinsically conductive (or can be made so by doping) or by loading an electrically insulating matrix with a conductive filler (carbon black, graphite fibers, metallic powders, etc.).[1] When exposed to vapor phase analytes these conducting composites exhibit good sensibility through a drastic increase in their resistance. [1] The behavior of conductive composite in presence of organic vapor has been described on the basis of percolation theory.[1] The sensor response is function of the amount organic vapor absorbed in polymer matrix and the content of filler present in polymeric composite.[2]

Many experiments show that percolation threshold is dependent on diameter of particles. The threshold is lower when the size of particles is smaller.[3] The same behavior is also observed with filler with high aspect ratio.[4] For example the use of carbon nanotubes in polymer composites is found to reduce the percolation threshold to a much lower filler

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volume than in the case of a carbon black/polymer matrix.[5] In this work we want to understand also the influences on the performances of the corresponding sensors.

We have fabricated films of polymeric composites using different fillers all made of carbon, but with different particle sizes (from micrometers to nanometers), structure and chemical functionalization. In particular, we have used commercial carbon blacks, single and multi-walled carbon nanotubes. We produce thin conductive films characterized by different grade of dispersion of conductive filler in polymer matrix: poly(methyl-methacrylate), poly (2 hydroxy-ethyl-methacrylate) or atactic poly(styrene).

In order to improve the dispersion of the filler in the polymeric solution we have modified commercial carbon black by a Fenton type oxidation. We study filler size distribution in polymer solution by dynamic light scattering and filler dispersion in final film by optical microscopy. This has allowed to investigate about the influence of different fabrication parameters on film morphologies (homogeneity, grade of filler dispersion, size of filler aggregates) and conductivity. Testing to different VOCs the sensor devices, will show the influence of different morphology on the characteristics of the sensors responses.

Experimental part

The fabrication process of thin film composite vapor sensing device we have chosen is reported in Figure 1 while the fillers and the polymers used in this work are summarized in Table 1. Black Pearls 2000 modified by a Fenton type oxidation (Mod-CB) has been prepared using an acid aqueous solution of H_2O_2 (30%) and $FeCl_3$ in a sonicating bath. Soot is a home made filler produced by acetylene synthesis [6] but without any purification process. This filler is interesting because it is easily fabricated, however it is mixed with impurity characterized (by Fourier transformed infrared spectroscopy) as silicon substrate particles.

Multi -wall (MW-CNT) and single-wall (SW-CNT) carbon nanotubes have been prepared by M. Teresa Martinez and colleagues and obtained by arc discharge.[7] SW-CNTs have a diameter of 1.2÷1.8 nm while length is in the order of microns. MW-CNTs, made of concentric SW, show an external diameter of 2÷25 nm and an internal diameter of 1÷3 nm.

The polymer/solvent solutions of 0.4% by weight concentration (see Table 1) are prepared dissolving polymer in the proper solvent (tetrahydrofuran or ethanol). We used the following polymers: Poly(methyl-methacrylate), Poly(2 hydroxy-ethyl-methacrylate), and

two types of atactic poly(styrene) of different molecular masses. The solvents (reagent grade) and the polymers used in this study were used as received.

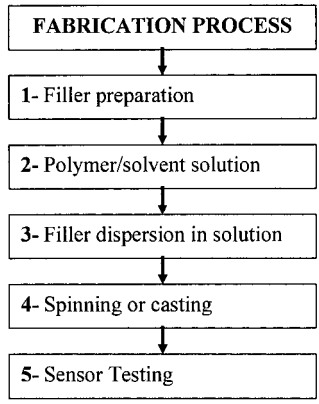

Figure 1. Fabrication process flow chart for sensor based on film of polymeric composite.

Table 1. Polymers and fillers used to prepare composite films.

FILLERS		POLYMERS			
Name	**Symbol**	**Name**	**Symbol**	**M_w (g/mol)**	**Solvent**
Cabot Commercial carbon black (Black Pearls 2000)	CB	**Atactic polystyrene** (Dow)	l-PS	117000	Tetrahydrofuran (THF)
Black Pearls 2000 modified by Fenton type oxidation	Mod-CB	**Atactic polystyrene** (Aldrich)	h-PS	350000	Tetrahydrofuran (THF)
Soot obtained by acetylene synthesis	S	**Poly(methyl-methacrylate)** (Aldrich)	PMMA	300000	Tetrahydrofuran (THF)
Multi-Wall nanotubes	MW-NT	**Poly (2-hydroxy ethyl methacrylate)** (Aldrich)	PHEMA	120000	Ethanol
Single Wall nanotubes	SW-NT				

The dispersion of the filler in the solution has been obtained by ultrasonic bath for 90 minutes. The amount of filler used to produce suspension is approximately 25% by weight for all types of fillers except carbon nanotubes (10% by weight). All suspensions have been characterized at different times by Dynamic Laser Scattering (DLS) using a HPPS 3.1

(Malvern Instruments). DLS and optical analysis have allowed to study the particle size distribution of fillers and dispersion time stability.

The last step (Figure1) is the realization of the sensing devices by spinning or casting on substrate. All suspensions are deposited drop by drop on the spinning substrate (glass of $2x2cm^2$) except suspensions of nanotubes deposited by casting. The thin films of composites have been characterized by Tencor P10 surface profiler and optical analysis (Polyvar Met, Reichert-Jung). Film thicknesses are in the submicrometer range as pointed out by Tencor P10 surface profiler.

The sensing devices responses to acetone and ethanol have been studied using a Gas Sensor Characterization System (GSCS) described in a previous work. [6]

Results and discussion

Table 2 shows some results of DLS characterization of suspensions prepared dispersing conductive fillers in different polymer solutions. We study polymers characterized from different polarity: poly(2-hydroxy-ethyl-methacrylate) (PHEMA), poly(methyl-methacrylate) (PMMA) and atactic polystyrene (h-PS). It is possible to observe that the average size of commercial carbon black (CB) increases when more polar polymer/solvent system is used. The lowest sizes are obtained with a no polar h-PS (compared data of suspensions number 1, 3, 8). Similar results are individuated when we have used no refined soot (Table 1, samples 5, 9). All suspensions (out of sample 1, Table 1) have shown a very good time stability, at least few weeks.

The quality of filler dispersion is strictly related to the interaction between the filler, polymer and solvent. In order to improve the dispersion of the filler in the PMMA and PHEMA solutions we have modified commercial carbon black by a Fenton type oxidation. This method has allowed to obtain both better filler dispersion and time stability of CB in the solutions as suggested by DLS analysis (compare in Table 1, samples number 1-2 and 3-4). Anyway a Fenton type oxidation has given good results especially when using polymers requiring polar solvents (samples 1-2).

Dispersion of the nanotubes in the solvent has been difficult due to the strong interaction between the nanotubes. For this reason we could execute only DLS analysis on the surnatant phase that has been successively used for the casting deposition of the composite films (see table 1 samples 6-7).

Table 2. Results of Dynamic light scattering (DLS) analysis made on suspensions obtained adding filler in polymer solution.

Suspension Characteristic				Average Size (nm)
Number	**Polymer**	**Solvent**	**Filler**	
1	PHEMA	Ethanol	CB	4033
2	PHEMA	Ethanol	Mod-CB	408
3	PMMA	THF	CB	291
4	PMMA	THF	Mod-CB	260
5	PMMA	THF	S	722
6	PMMA	THF	*MW-NT	270
7	PMMA	THF	*SW-NT	290
8	h-a-PS	THF	CB	206
9	h-a-PS	THF	S	403

*surnatant phase.

Figure 2 shows the morphology of CB composites obtained with similar methods of preparation and spinning deposition of suspension. The optical images of film confirm the observations extracted from the data DLS. A more homogeneous dispersion of CB aggregate is present in films obtained with a-PS matrices (Figure 2, a-b). This corresponds at lower initial resistivities and more sensitivities to acetone of corresponding sensors (Figure 3). The response to ethanol is instead negligible because apolar PS samples have a little capacity to adsorb the polar vapors of ethanol.

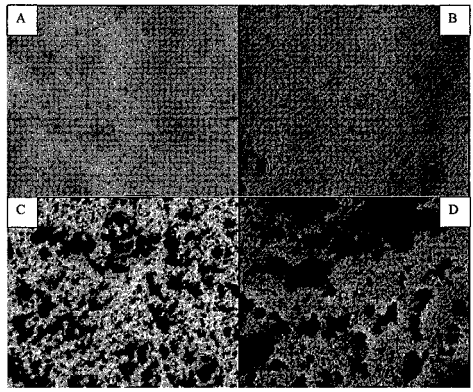

Figure 2. Typical morphologies of the four film types of CB composites obtained by optical micrography at low magnification (100x): a) l-PS/CB (R_o=61KΩ), b) h-PS/CB (Ro=170KΩ), c) PMMA/CB (Ro=8KΩ), d) PHEMA/CB (Ro=79KΩ). Ro is the resistance measured before exposition to vapor solvent.

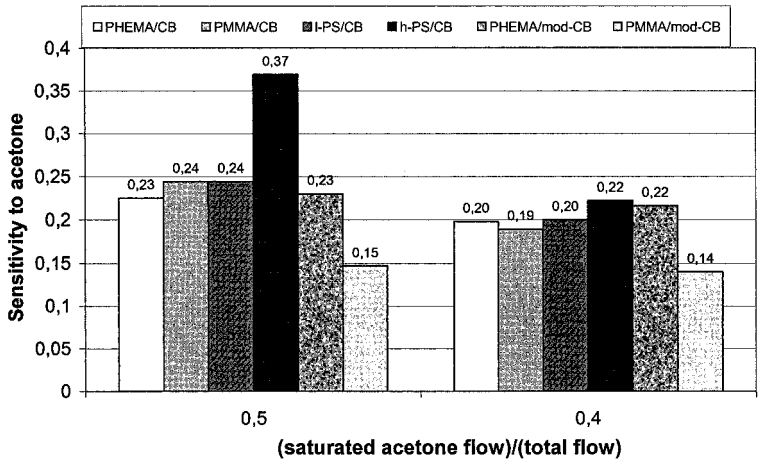

Figure 3. Response to acetone of sensors based on CB composites. Acetone concentration is 0.5% and 0.4% of its vapor pressure at environment temperature. Sensitivity is calculated as (Rmax-Ro)/Ro from the dynamic responses.

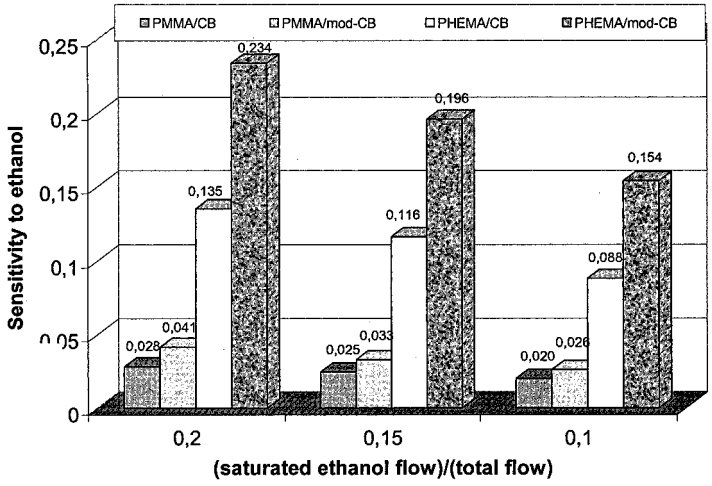

Figure 4. Response to ethanol of sensor based on CB composites. Acetone concentration is 0.1%, 0.15% and 0.2% of its vapor pressure at environment temperature. Sensitivity is calculated as (Rmax-Ro)/Ro from the dynamic responses.

Figure 4 compares the responses to ethanol of sensors obtained with PMMA and PHEMA with CB and Mod-CB. How it is expected the sensors based on PHEMA exhibit an higher response. Moreover for both the polymer matrices is possible to observe a further enhancement of the responses when we use mod-CB as filler. Generally the response times of sensors based on mod-CB are higher than corresponding sensor made with CB composite. This probably is related to low porosity of the composite film.

In figure 5 the response to acetone of sensing devices obtained with PMMA nanostructured fillers is compared with PMMA/CB sensor. Sensitivities of PMMA/MW-CNT and PMMA/SW-CNT are generally interesting especially at high acetone concentrations but further study is needed to optimize the response times.

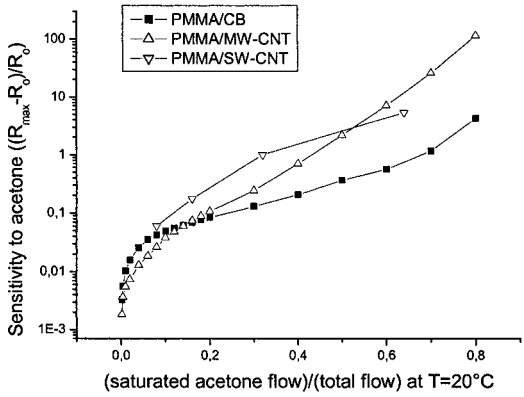

Figure 5. Responses to acetone of sensor based on PMMA composites. Acetone concentration sweep the range 0.2%-80% of its vapor pressure at T=20°C. Sensitivity is calculated as (Rmax-Ro)/Ro from the dynamic responses.

Conclusion

We have prepared thin film composites using different commercial carbon blacks and nanostructured fillers, realizing and characterizing the relative sensing devices.

Filler dispersion in the polymer/solvent solution has shown to be a critical step to obtain homogeneous sensing films. However, responses to organic vapor of sensing devices are strongly dependent on more parameters, generally related to filler-polymer interaction.

Composites made of carbon nanotubes are promising materials for sensing devices but require further work especially to learn to control their dispersion in the polymeric matrix.

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