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Gas sensing properties of conductive polymer nanocomposites

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Abstract

Nanocomposites consisted of carbon nanotubes (CNT) dispersed in various polymer matrices were prepared for the investigation of their sensing properties. The results from morphology study and electrical/dielectric characterization showed good dispersion of the filler with low percolation threshold. The response to water and ethanol vapour, at different concentration, was also studied showing better response for the more hydrophilic polymers and those with glass transition temperature below room temperature.

Keywords gas sensors, conductivity, polymer nanocomposites, carbon nanotu

1. Introduction

Polymers are a very attractive class of materials for use in sensor applications due to the fact that their chemical and physical properties may be tailored over a wide range of characteristics[1]. The above possibilities are enormously expanded by the latest grow of nanotechnology and the emergence of a new class of nanocomposite materials with improved properties. The incorporation of carbon nanotubes(CNT) into a polymer matrix in order to prepare conductive nanocomposites appear also as a very promising direction to prepare active elements for gas sensors [2]. For conductivity type gas sensors, the active material of the sensor should have adequate electrical conductivity at low CNT content. The major prerequisite for the latter is the good dispersion of CNT in the polymer matrix which is strongly dependent on the polymer-CNT interactions. PMMA has been proven to be an easy processable polymer which lead to nanocomposites with low percolation threshold[3,4]. In this work results on the influence of different filler content and a comparison of various polymer matrices for gas sensing applications are presented.

2. Experimental

Conductive polymer nanocomposites were prepared by dispersing multiwalled carbon nanotubes in the polymer solution by ultrasonication. Unmodified CNT and functionalized CNT (f-CNT) with carboxyl groups were used as conductive nanofillers. Various matrices with different glass transition temperatures and hydrophilicity were used

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for the prepapration of the nanocomposites as indicated in Table 1. Electrical conductivity of films deposited on either brass electrodes or glass substrates was measured by both ac and dc techniques described in [4] and the percolation threshold for the PMMA/f-CNT was determined after analyzing the results on samples with varying filler content. The gas sensors were realized by depositing thin films of the nanocomposites on copper interdigitated electrodes of a printed circuit board by solution casting.

The concentration of the target vapor in the measurement cell was adjusted by a set-up (Fig.1) allowing controlled evaporation and mixing of the desired liquid with the purge gas (nitrogen). The response of the sensors to ethanol and water vapor was examined by measuring the change in electrical resistance of the prepared thin films at room temperature. For water uptake measurements with gravimetric technique an IGAsorp humidity sorption analyzer was used[5].

Table 1. Polymer matrices used in the study, their glass transition temperature (T_g), water uptake (h) at 98% relative humidity, the respective solvent used and conductivity σ of nanocomposites with 5wt% filler content.

Polymer matrix	T_g (°C)	h at 98 % r.h.	Solvent	Nanocomposite	σ (S/cm)
PMMA poly(methyl methacrylate)	105	2 %	THF	PMMA/5%CNT	$5{,}9\cdot10^{-1}$
				PMMA/5%f-CNT	$5{,}6\cdot10^{-3}$
PS poly(styrene)	95	0,4 %	toluene	PS/5%f-CNT	$4{,}1\cdot10^{-2}$
PEA poly(ethyl acrylate)	-15	2 %	THF	PEA/5%CNT	$4{,}3\cdot10^{-1}$
				PEA/5%f-CNT	$5{,}7\cdot10^{-3}$
PMA poly(methyl acrylate)	15	3 %	THF	PMA/5%CNT	$3{,}4\cdot10^{-1}$
				PMA/5%f-CNT	$3{,}2\cdot10^{-3}$
PVP poly(vinylpyrrolidone)	185	50 %	water	PVP/5%CNT	$1{,}6\cdot10^{-3}$
				PVP/5%f-CNT	$<1\cdot10^{-7}$
PAA poly(acrilic acid)	105	60 %	water	PAA/5%CNT	$1{,}9\cdot10^{-2}$
				PAA/5%f-CNT	$8{,}1\cdot10^{-5}$

3. Results and discussion

In Fig. 2 the maximum relative resistance change $(R-R_o)/R_o$ upon exposure to 30% relative humidity level (r h) of PMMA/CNT nanocomposites with 5%wt unmodified and functionalized CNT as well as for 20% wt of carbon black (CB) is depicted. The results showed better response for nanocomposites with f-CNT. The same behavior was also observed for nanocomposites with the other polymer matrices which were tested at various r.h. and ethanol concentrations. Based on the above results, the use of f-CNT was chosen to further study the influence of filler content of nanocomposites on gas sensing properties.

It is known that the increase of the resistance of nanocomposites with conductive fillers upon exposure to volatile gases is attributed to the destruction of the conductive filler network due to polymer swelling [3]. In that sense, the connectivity of the above network is of great importance for gas sensing applications. The use of f-CNT leads to nanocomposites with improved filler dispersion and distribution as revealed by morphology studies [6]. Percolation threshold for the PMMA/f-CNT was estimated to be 0.21%wt. The above low value provides an additional indication of good dispersion of f-CNT in the polymer matrix. In Fig. 3 the response of nanocomposites with different filler content is examined. The nanocomposites with lower content of f-CNT showed better response towards ethanol but considerable scattering for high relative humidities. The instability of PMMA/f-CNT nanocomposites with f-CNT content close to percolation threshold at high r h must be taken into account for practical sensor applications. The nanocomposite with 5%f-CNT being well above percolation threshold gave stable measurements with adequate high responses. The typical response of PMMA/5%f-CNT towards different ethanol concentration is presented in Fig. 4. A monitonically increase of $(R-R_o)/R_o$ is observed upon exposure to the target gas which is restored to the initial value upon removal of the analyte and purging with nitrogen. Reversibility and reproducibility (inset of Fig.4) of the

response was also observed. Based on the above results a filler content of 5%f-CNT was chosen for the study of the influence of different polymer matrix on sensing properties.

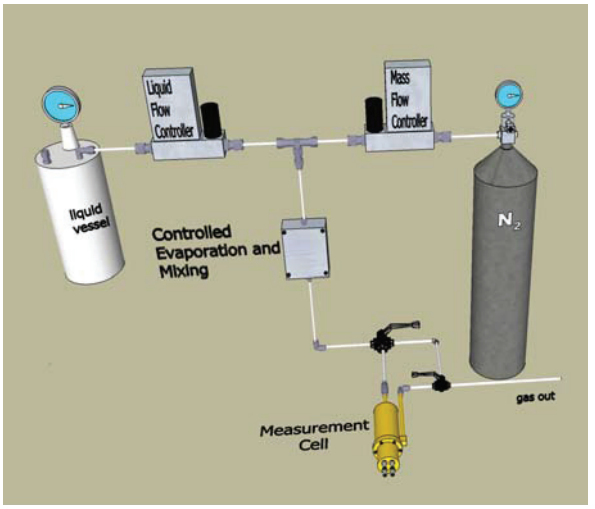

Fig. 1. Experimental set-up for gas sensors testing.

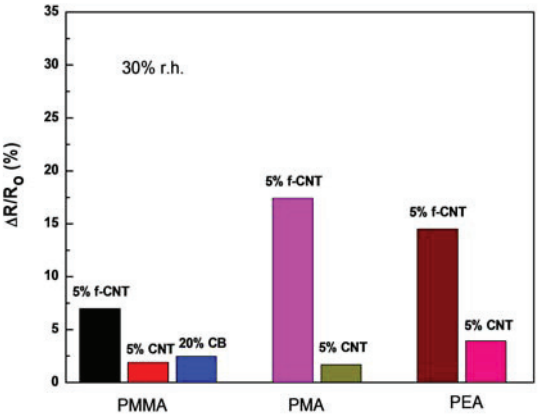

Fig. 2. Maximum response for nanocomposites shown on plot with different fillers at 30%r.h

In Fig. 5 the comparison of different polymer matrices with 5% f-CNT at various different r.h. levels is depicted. The nanocomposites with the more hydrophilic polymers present significantly higher responses towards water vapour especially at high r h. In order to have an estimate for the response times of the nanocomposites with different polymer matrices the time to reach 90% of maximum $(R-R_o)/R_o$ at 30%r.h. was determined. The response time for PEA/5% f-CNT was less than 10 sec, while for PMMA/5% f-CNT and PS/5% f-CNT was 20 and 40 sec, respectively. For the nanocomposites with more hydrophilic polymers, PVP/5%CNT and PAA/5%f-CNT, the response times were evaluated to be 40 and 160 sec, respectively. The above results indicate that the quicker response was observed for the nanocomposite with PEA being in the rubbery state at room temperature.

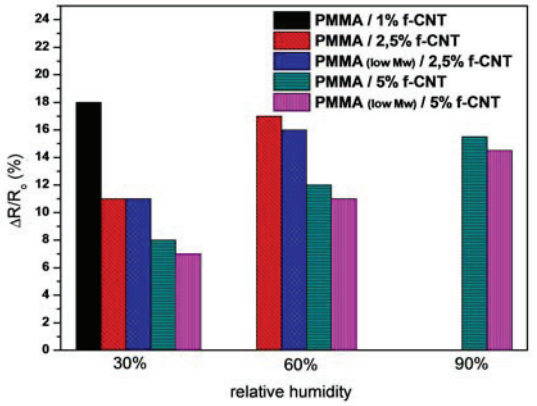

Fig. 3. Maximum response for PMMA/f-CNT nanocomposites at different relative humidity levels.

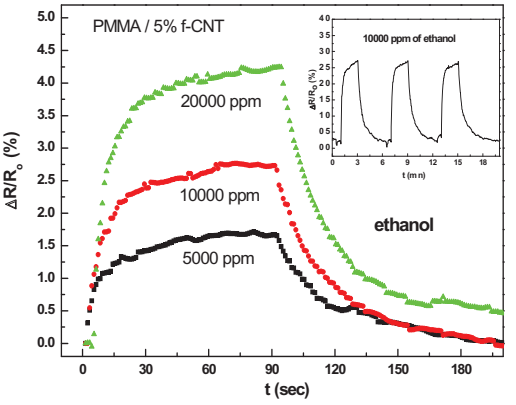

Fig. 4. Response of PMMA/5%f-CNT to different concentrations of ethanol. Inset shows the repeatability of the response.

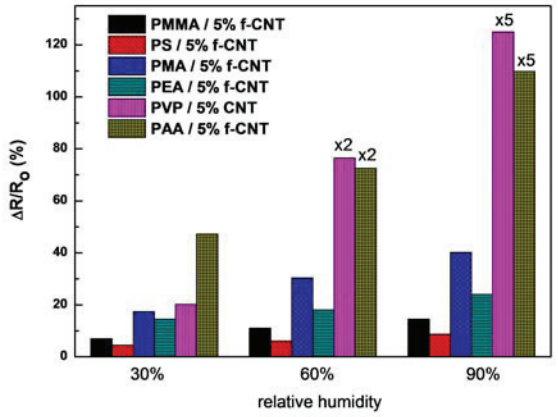

Fig. 5. Maximum response for the nanocomposites at three different relative humidity levels.

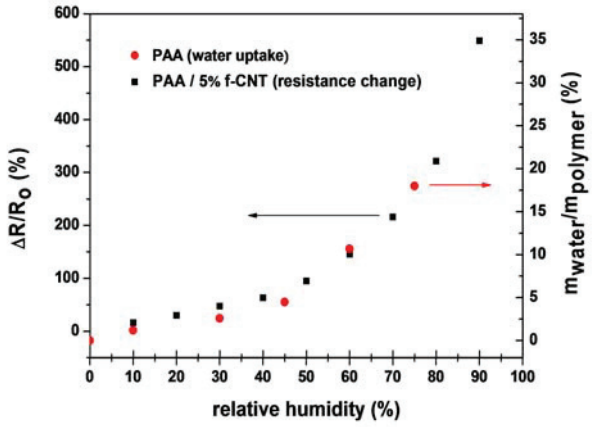

Fig. 6. Maximum resistance change of PAA/5%f-CNT and water uptake measured gravimetrically of PAA against relative humidity.

In Fig. 6 the maximum relative resistance change of PAA/5%CNT together with water uptake of pure PAA measured gravimetrically against relative humidity is depicted. The two curves present very similar trend indicating that f-CNT act as sensitive probes of the polymer matrix swelling. The above correlation is of great interest and measurements to further explore that behaviour also for other polymer matrices are in progress.

4. Conclusions

The results showed that solution mixing by ultrasonication is an effective technique for dispersing carbon nanotubes in a polymer matrix leading to nanocomposites with low percolation threshold. The study of the percolation threshold is important for the determination of an optimal filler concentration for gas sensing applications. Nanocomposites with f-CNT showed better response than those with unmodified ones. CNT content should be well above percolation threshold in order to have lower signal to noise ratio. Nanocomposites with hydrophilic matrices showed higher response to water and ethanol while matrices with lower glass transition temperature showed faster response.

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