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PROPERTIES OF MULTIFUNCTIONAL POLYMERS — CARBON BLACK COMPOSITE VAPOR DETECTORS

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Abstract. In this work the electrical properties of vapor detectors, formed from composites of conductive carbon-black and insulating organic multifunctional polymers having metal ions complexing ability, were investigated. The new composites are tailored to produce increased sensitivity toward specific classes of analyte vapors. Resonant frequency shift of a Quartz Crystal Microbalance (QCM) and dc resistance measurements have been also performed simultaneously on polymer-carbon black composite materials. For comparison purpose, poly(vinyl chloride) (PVC) with di(2-ethylhexyl)phthalate (DOP), a traditional low molecular weight plasticizer, is used as a representative of the behaviour of a traditional composite vapor detector. These new detectors showed an enhanced sensitivity upon exposure to acetic acid and amines vapors; the performances of our systems are 10^3 times higher than those of a traditional composite vapor detector. Moreover the extent of such responses is beyond that expected by mass uptake upon exposure to the same vapors and cannot be attributed solely to differences in polymer/gas partition coefficients. In this respect, several different chemical factors determine the dc electrical response of this system: in our opinion changes in polymer conformation during the adsorption process also play a significant role. The effects of the temperature on the electric resistance of the vapor detectors have also been studied. These materials showed a discontinuity in the temperature dependence of their resistance, and this discontinuity provided a simple method for determining the T_g of the composites.

Keywords: vapor detector, multifunctional polymer, sensitivity, selectivity, composite, glass transition temperature.

1. Introduction

Arrays of broadly responsive detectors have been used for many years as means of detecting a wide range of vapors. These systems have been proposed in several fields for identification, classification and quantification of analyte vapors. Chemically sensitive resistors fabricated from conductive fillers dispersed into insulating organic polymers are an attractive implementation of this approach [1-4]. A variety of composites, actually, can be easily obtained and used to realize arrays of chemically different resistive detectors, using inexpensive starting materials and equipment. The behaviour briefly suggests that they can be regarded as promising gas sensors characterized by easy processability and cost effectiveness.

The conductivity of these composite systems can be understood in terms of the percolation theory [5]. At low concentrations, generally, the filler incorporated in the form of small particles with a different shape, is distributed homogeneously in the volume of the insulating matrix, and there are no contacts between adjacent particles. With rising filler concentration, agglomerates of the filler particles start to form because the particles are in contact with each other. At a certain critical volume of this conductive filler, called percolation threshold, the growing agglomerates reach a size which makes possible to touch each other and in this way a continuous conducting network through the polymer matrix is formed. As a consequence of the first appearance of the network, the composite transforms from an insulator to a conductor.

Exposure of such a composite film to an organic vapors increases its resistivity because of the variation of the matrix volume fraction with respect to the conductive phase. Carbon black, Ag, Cu or conductive organic polymers have all been used as the conductive phase.

It is known from literature that another approach to obtain sensor diversity, involving modifications of the properties of a base polymer vapor detector, is attained through the addition of plasticizers. In such a way, several polymeric matrices and traditional low molecular weight plasticizers have been employed [6].

An interesting alternative might be represented by polymeric blends containing a low glass transition temperature (T_g) polymer, possessing high miscibility with the matrix [7]. The main advantage of such systems would

be that drifting phenomena typical of low molecular weight plasticizers could be avoided. In addition, the properties of these sensors might be tuned by varying the plasticizer molecular weight.

The basic performance properties of such arrays, including detection limits and responses to mixtures of analytes have been described in literature [1, 2, 8-10].

Moreover recent studies are devoted to the development of chemiresistive vapor detectors with increased sensitivity towards analyte vapors [11-13].

In this context we studied new series of carbon black multifunctional polymers composites based on poly(amidoamine)s (PAAs) which show large enhancements in sensitivity towards specific classes of analytes such as amines and carboxylic acid vapors [14, 15]. In particular these materials have a sensitivity 10^3 higher than the performance of typical insulating polymer carbon black composite vapor detector. Compositional diversity in an array of such vapor detectors, can be achieved by varying the chemical structure of monomers. Nevertheless, having PAAs excellent metal ions complexing ability, diversity in the response behaviour could also be obtained by chelating different heavy metal ions to the same carbon black polymer composite.

The carboxylic acid and amines vapor detection properties of PAA based materials, have been compared with the detection properties of lower polarity analytes, such as acetone and pentane.

For comparison purposes, a conducting carbon black-polymer composite detector based on poly(vinyl chloride) (PVC), as the base polymer, with the addition of di(2-ethylhexyl)phthalate (DOP), a typical low molecular weight plasticizer, was prepared and checked with all the analytes considered.

The goal of this work is to investigate whether it is possible, through the choice of the polymeric component of the carbon black polymer composite detector, to achieve enhanced sensitivity to a specific class of analyte vapors and to explore the mechanism by which these detectors achieve their enhanced sensitivity. Finally the effects of the temperature on the electric resistance of the vapor detectors have also been studied and it provided a simple method for determining the T_g of the composites.

2. Experimental

2.1. Materials

All the solvents used to generate analyte vapors were reagent grade and were used as received (Aldrich Co Milan, Italy); poly(vinyl chloride) (PVC) and di(2-ethilhexyl)phthatate (DOP) were purchased from Aldrich Co (Milan, Italy).

2.2. Preparation of the Conductive Films

Two PAAs BAC-DMEDA and BAC-EDDA synthesized as previously described [14], and PVC plasticized with DOP were used in this work. The conductive films were obtained by spray from a suspension prepared as follows: 80 mg of organic matrix (PAAs or PVC with 40 % by weight of DOP) were dissolved in 10 ml of the solvent (water or tetrahydrofurane respectively) and 20 mg of carbon black were added. The mixture was sonicated for 5 min and therefore it was sprayed on a Quartz Crystal Microbalance (QCM) element until obtaining a frequency shift of about 20 kHz. The films were dried in the air for 24 h before use.

The same procedure was followed to prepare films with PAAs complexing heavy metal ions. Those systems were obtained adding to the water solution, at pH 7.5, 15 wt % (by weight of the PAA) of Cu^{++} or Co^{++}.

2.3. Data Collection and Analysis

The calorimetric analyses of the composites were performed using a Digital Scanning Calorimeter (DSC) Q100 TA Instruments, interrelated with a TA Control Instrument Q Series.

QCM crystals (AT-cut, 6MHz, blank diameter is 13.5 mm, electrode diameter is 7.8 mm) with the custom electrode pattern were obtained from Elettroquarz S.r.l. (Milan, Italy). Frequency shift measurements were performed on carbon black polymer films in conjunction with simultaneous resistance measurements of these composite vapour detectors by means of an electrode configuration in which the standard QCM oscillation electrodes were at 90° angles to make a room for two additional resistance tabs [8, 16]. The QCM technique is based on detection the mass at the surface of the quartz crystal by measuring the change of the crystal oscillation frequency. The interaction of detectors with different analyte vapors on a surface of the crystal resulted in the increase of the crystal mass and in the decrease of the oscillation frequency.

The measurements were carried out with a Laybold Inficon XTM/2 oscillator and frequency counter (East Syracuse, NY) and an APPA model 305 digital multimeter (Taiwan), both equipped with a LabView 6.0 acquisition system running on a Pentium III personal computer.

The frequency shift and the resistance response of each modified QCM sensor were measured as a function of time under exposition to different organic vapours. Each sensor was first placed into the sensing thermostatic chamber (volume = 0.604 l) equipped with a thermocouple, and then it was kept under a nitrogen stream (1 l/min) until steady state values of resistance and frequency were observed. Finally, the frequency and the resistance were sampled for 20 min more under static condition to obtain

the baselines. All measurements were run in nitrogen, at 297.15 K, under static condition. All analytes were injected into the chamber and exposed to the detectors for 900 s, and then nitrogen was passed over the composite for 900 s maintaining a flow rate of 1 l/min. The adsorption and desorption cycles were repeated more times, increasing the vapour concentration in step of 4.9 ppth for acetone, 4.4 ppth for pentane, 6.5 ppm for 1-butylamine, 4.7 ppm for triethylamine and 1.14 ppm for acetic acid.

3. Results and Discussion

PAAs are regular amide polymers characterized by the presence of amido and tertiary amino groups regularly arranged along their macromolecular chain. They are obtained, in a linear form, with a considerable variety of structures by stepwise polyaddition of primary monoamines or bis-secondary amines, to bis-acrylamides [17]. PAAs are hydrophilic, water-soluble, generally characterized by moderately basic properties and high capacities to complex metal ions.

PAAs carrying additional functions (carboxyl, hydroxyl and amine) as side substituents can be easily obtained, starting from the appropriate monomers. These polymers have been extensively studied because the versatility of their chemical structures allows a variety of applications. In particular they were proposed as a drug carrier in the biomedical field, and in the environmental engineering for their heavy metal ions chelating properties [15, 17-19].

Two structurally related PAAs namely BAC-DMEDA and BAC-EDDA, which, in the linear form, have been shown to possess the capacity to form stable complexes with well-defined stoichiometry, were selected for this study. The products were prepared as previously reported [14] and characterized in terms of molecular weights and molecular weight distributions by analytical Gel Permeation Chromatography (Table 1), making use of PAAs purposely prepared and analysed by NMR techniques.

The conductive composite detectors were obtained by spraying a suspension prepared by dissolving the polymer materials in water and adding the conductive filler. In order to explore the mechanism by which these detectors work, all sensors were tested upon exposure to different organic vapors using a modified QCM crystal in which the resonant frequency shift and dc resistance responses were performed simultaneously. Since the interaction between composite films with specific classes of analyte vapors on the surface of crystal produces an increase of the crystal mass, a corresponding decrease of the oscillation frequency was detected.

It was found that the new materials can detect the presence of gas by reversible variations in electrical properties. They showed high efficiency since they adsorb and desorb rapidly at room temperature and have a considerable endurance to continuous and repeated adsorption and desorption cycles.
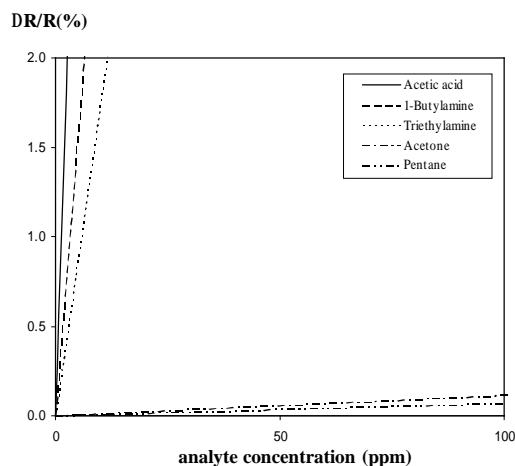
Fig. 1 presents the normalized resistance increase of a PAA-carbon black composite detector to various concentrations of volatile organic vapors having different polarity. The responses of new detectors showed high selectivity for different classes of analytes for example amines, alkanes or ketones. In particular the minimal amine as well as carboxylic acid vapour amount that they can detect is part per million (ppm), while the detection limit for other analytes with a lower polarity is part per thousands (ppth). This behaviour should be due to the chemical structure of the PAAs: both BAC-DMEDA and BAC-EDDA, actually, have a rather complex chemical structure with many polar groups arranged along the macromolecular chain and functional groups as side substituents which provide strong interactions with polar analyte vapors. Besides some analytes which produced enhanced sensitivity are reported in Figs. 2a and b, which show respectively the behaviour of BAC-EDDA and BAC-DMEDA. Each analyte produced a distinct response that was different from the response curve of every other analyte investigated. It was also possible to appreciate a diversification of the response curves against primary to tertiary amine. In this way it is possible to suppose a good selectivity of PAA-carbon black composite detectors even within the same analyte vapor family.
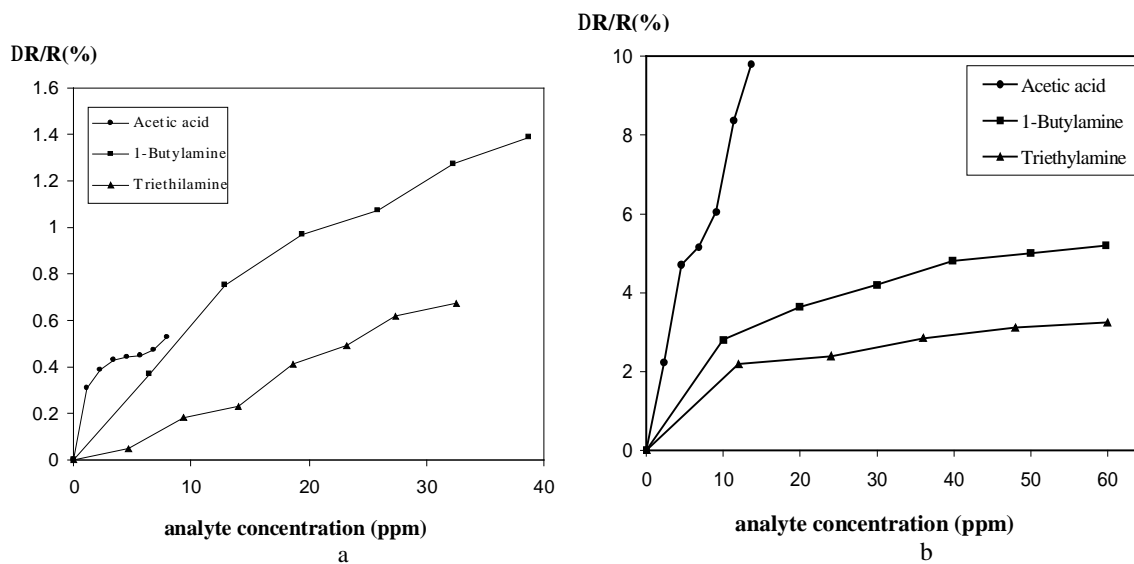
Table 1

Polymer structure, viscosity, molecular weights and T_g

| Structure	$h_{sp}/C^{a)}$,dl/g	$\overline{M}_w$, g/mol	$\overline{M}_n$, g/mol	T_g, K
[structure diagram] BAC-DMEDA	0.12	6050	4820	372.15
[structure diagram] BAC-EDDA	0.10	6900	5900	395.15

a) C= 0.2 % in NaCl 0.1 M

Fig. 1. Normalized resistance increase upon exposure for 900 s (see experimental)
of [BAC-DMEDA]Cu to increasing concentrations of different analytes

Fig. 2. Comparison of the resistance responses to increasing concentrations
of different analytes for: [BAC-EDDA]Cu (a) and [BAC-DMEDA]Cu (b)
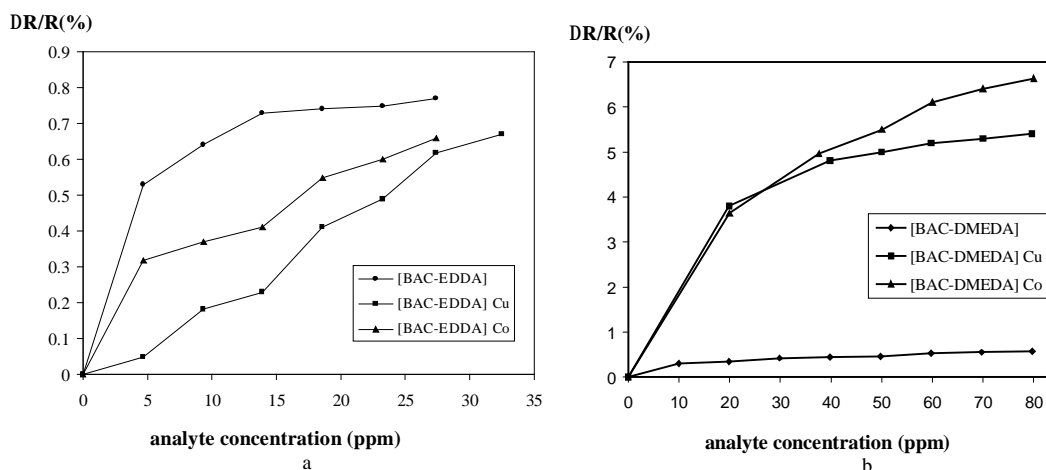
Fig. 3. Comparison of the resistance responses under triethylamine vapour exposition for 900 s (see experimental) of: [BAC-EDDA],
[BAC-EDDA]Cu and [BAC-EDDA]Co (a); [BAC-DMEDA], [BAC-DMEDA]Cu and [BAC-DMEDA]Co (b)

The behaviour of PAA composite film when exposed to above gases was compared to the relative differential resistance behaviour of PVC-DOP composite film, representative of the traditional materials used up to now for such application. The PAA composite detector clearly exhibited a significantly enhanced sensitivity as compared to other polymer composite detector films. Generally the new material can detect a mean value of amines or acetic acid concentration approximately 1000 fold smaller than that of PVC/DOP detector, in the same experimental conditions (prepared with the same filler and deposited in the same way on identical substrate) for the same analyte exposure.

As above reported, different chemical PAA structures also carrying additional functions as side substituents can be easily obtained starting from the appropriate monomers. These can be used as the insulating component to fabricate a variety of chemiresistive composite vapor detectors. Both PAA based detectors selected for this study showed enhanced sensitivity and selectivity to acetic acid and amines compared to other organic vapors.

Moreover a chemical diversification can be easily obtained by complexing different heavy metal ions on polymeric chains. In particular PAA's functional groups can act as ligands with heavy metal ions or provide strong interactions with other polar molecules. The complexation in water solution brings each monomeric unit to coordinate a metal ion, to give a more compact polymeric structure. The use of heavy metal ions produces chemical diversity in chemiresistive vapor detector improving the selectivity while maintaining the high overall sensitivity of the PAA based composites for specific classes of analytes. On this subject Fig. 3 presents the normalized resistance increase upon exposure to triethylamine vapor for respectively [BAC-EDDA] (Fig. 3a) and [BAC-DMEDA] (Fig. 3b) polymer free and the same structures chelating Cu^{++} and Co^{++} as model ions. Each detector produced a distinct response that was differentiable from the response curve of the other investigated ones. Besides, Fig. 3b shows that the presence of chelated metal ions on [BAC-DMEDA] allowed the sensors to amplify the response in terms of percentage variation of resistance.

The simultaneous measurements of QCM frequency shifts and resistance changes were performed to determine the underlying cause for the enhanced sensitivity of PAA based materials to organic acids or amines compared to low polarity organic vapors. Fig. 4 presents the resistance response of [BAC-EDDA]Cu vapor detector upon sorption and desorption cycles of 1-butylamine. The sorption steps were obtained by injection of increasing amount of analyte while nitrogen was passed over the detector to obtain desorption. The data indicate that the dc resistance change is directly related to the analyte concentration. Moreover these data fit well to a linear dependence of normalized resistance increase on analyte concentration also at ppm level as reported in insert of Fig. 4 at an expanded scale.

The corresponding frequency shift measurements are reported in Fig. 5. It can be observed that up to at least 40 ppm (cycles **a** to **f**) there is no significant trend in the frequency shift that can be related to the increase in analyte concentration. Only when the ppth level is reached (cycles **g** to **h**), the frequency shift shows a stepped response which scales with the concentration, demonstrating a detectable mass uptake in the cating film.
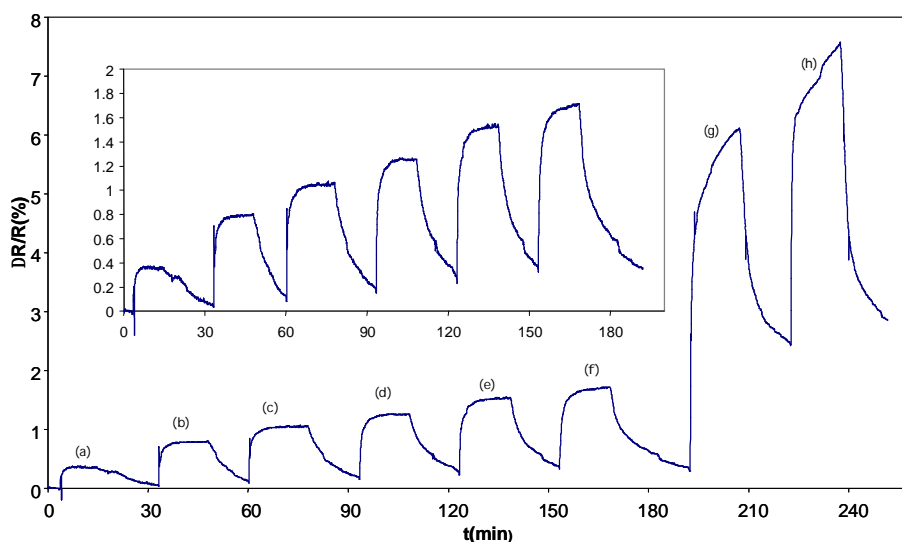
Fig. 4. Resistance response upon sorption and desorption cycles carried out on [BAC-EDDA]Cu composite sensor using the following concentrations of 1-butylamine: 6.5 ppm (a), 13 ppm (b), 19.5 ppm (c), 26 ppm (d), 32.5 ppm (e), 39 ppm (f), 1800 ppm (g) and 3600 ppm (h)

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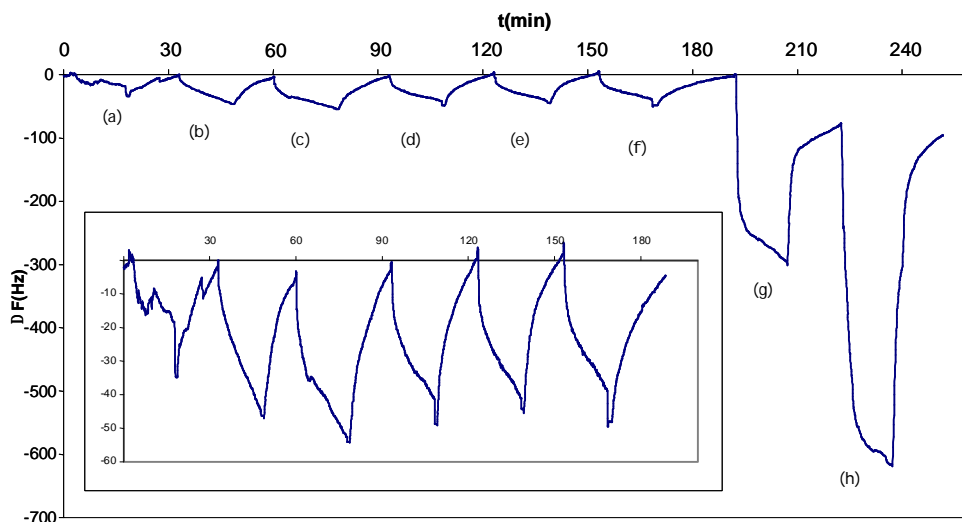
Fig. 5. Frequency shift response under sorption and desorption cycles carried out on [BAC-EDDA]Cu composite sensor using the following concentrations of 1-butylamine: 6.5 ppm (a), 13 ppm (b), 19.5 ppm (c), 26 ppm (d), 32.5 ppm (e), 39 ppm (f), 1800 ppm (g) and 3600 ppm (h)
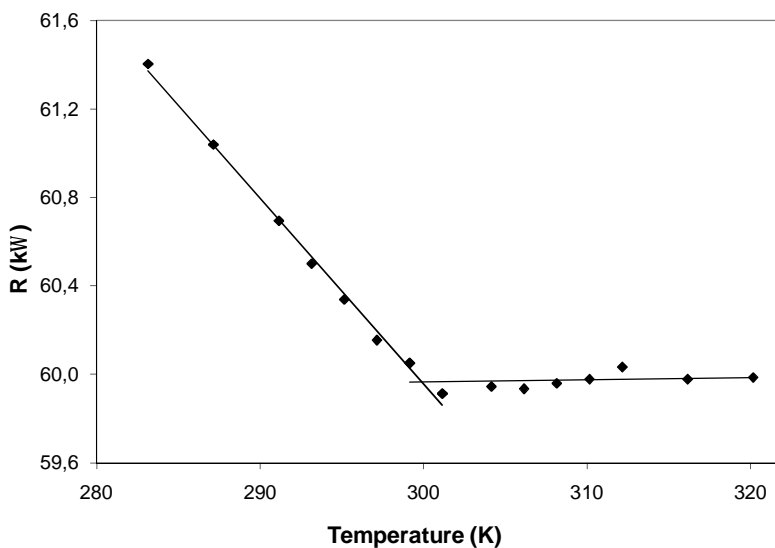
Fig. 6. Resistance of [BAC-DMEDA]Co as a function of temperature. The composite materials were heated from 283.15 K to 323.15 K at a rate of 0.1 K min^{-1}

Table 2

Comparison between T_g and T_d at the discontinuity point

Vapor detectors	T_g [a)], K	T_d [b)], K
[BAC-DMEDA]-CB	298.15	297.95
[BAC-DMEDA]Cu-CB	297.15	296.75
[BAC-DMEDA]Co-CB	299.15	299.95

[a)] Composite's T_g was evaluated using differential scanning calorimeter.
[b)] T_d is point of discontinuity evaluated in the temperature dependence of composites resistance curve.

The above studies have demonstrated that the higher sensitivity to amines as well as acetic acid cannot be attributed solely to the differences in polymer/gas partition coefficients, as it is for other organic vapors tested. The chemical structure of these polymers, characterized by the presence of specific groups regularly arranged along the macromolecular chain, strongly interact with target analytes. On the other hand this complex structure imparts rigidity and high organization in polymer packaging (*i.e.* hydrogen bonds). In this connection, we have recently demonstrated that the PAA ion chelation for example, occurring through a cyclic structure around the metal atoms, highly constrains polymer chains causing changes in molecular packing and suppressing segmental motions and T_g [20]. Small amounts of analyte vapors probably disarrange these constraints causing changes in molecular packing and determine the enhanced sensitivity and selectivity observed.

Since temperature influences vapor sorption and permeability, that effect changes in the dc electrical resistance response of polymeric detectors [21], measurements of electrical resistance of PAA carbon black composites were also performed at several temperatures. All samples showed a pronounced change in resistance as the temperature was varied, in particular a decrease of $\Delta R/R$ (%) with the increasing temperature was observed. In addition a discontinuity in the temperature dependence of the resistance was also generally highlighted. For example Fig. 6 displays the dc electrical resistance of [BAC-DMEDA]Co detector as a function of the temperature and the discontinuity formation approximately at 300.15 K.

On the other hand, the glass transition temperature (T_g) of the PAA composite detectors measured using differential scanning calorimeter, correlated very well with the discontinuity in the temperature dependence of the resistance (Table 2). This behavior is as expected considering that the phase change between glassy region below T_g and rubbery phase above T_g, produces a change in the connectivity of the network and consequently in the electrical conduction through the conductive filler.

This property of the carbon black composites can be exploited to a simple and inexpensive method to determine the glass transition temperature of composites, representing also a good indicator of the temperature above which the detector should be operated to obtain high diffusivities for analytes.

4. Conclusions

The use of multifunctional polymers as the insulating component in chemiresistive vapor detectors produces significant enhancements in sensitivity to amines and carboxylic acid vapors relatively to traditional polymers used for such application. Such PAA based detectors show selectivity toward the above vapors compared to other analytes with low polarity.

Sensor diversity is achieved varying the chemical structure of monomers as well as chelating different heavy metal ions to the same carbon black polymer composite. In both cases the high overall sensitivity of the PAA based composites for specific classes of analytes was maintained. The simultaneous measurements of frequency shifts and resistance changes have demonstrated that the higher sensitivity of these systems to amines and carboxylic acid cannot be attributed to the difference in polymer/gas partition coefficients. Although several different chemical factors determine the dc electrical response of this system, in our opinion changes in polymer conformation during the adsorption process play a significant role to produce the large increase in sensitivity. Moreover a discontinuity present in the temperature dependence of the materials resistance provides a simple method to determine the T_g of the carbon black composites.

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ВЛАСТИВОСТІ ДЕТЕКТОРІВ ПАРІВ НА ОСНОВІ КОМПОЗИТІВ БАГАТОФУНКЦІЙНИХ ПОЛІМЕРІВ–САЖА

Анотація. *Досліджено електричні властивості детекторів парів на основі композиту провідної сажі та ізоляційних органічних полімерів з йонами металів комплексоутворюючої дії. Створено нові композиційні матеріали для забезпечення підвищеної чутливості до конкретних класів аналізованої пари. Одночасно проведені вимірювання резонансної частоти зсуву кварцекристалічних мікроваг (QCM) і опору постійного струму для композитного матеріалу полімер-сажа. Для порівняння використаний традиційний низькомолекулярний пластифікатор полі(вінілхлорид) (PVC) з ді(2-етилгексіл)фталатом (DOP), який використовується у традиційному композитному детекторі парів. Нові детектори показали підвищену чутливість до дії оцтової кислоти і парів амінів; показники нової системи в 10^3 разів кращі за традиційні композитні детектори парів. Крім того, така чутливість виходить поза межі очікуваної при масовому поглинанні при дії на ту ж пару і не може бути віднесена виключно до відмінностей полімер/газового коефіцієнту розділу. В зв'язку з цим, декілька різних хімічних чинників визначають електричний відгук постійного електроструму цієї системи: в зміни в конформації полімеру в процесі адсорбції також відіграють значну роль. Вивчено вплив температури на електричний опір детекторів парів. Нові матеріали показали скачок (різку зміну) залежності температури від їх опору, і цей скачок забезпечує простий метод визначення температури склування композитів.*

Ключові слова: *детектор парів, багатофункціональний полімер, чутливість, селективність, композит, температура склування.*