Conductive Polymer-Composite Sensor for Gas Detection

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Abstract

Conductive polymers with carbon black filler were prepared for gas sensor application utilising ultrasonic mixing. The composite sensors were exposed to different types of gases and the resulting changes in the resistivity were recorded. The effects of ultrasonic mixing and sensitivity of the composite sensor to various organic gases were examined.

Keywords: gas sensor, carbon black, PMMA, ultrasonic, mixing

1   Introduction

There has been great interest in the study of conductive polymer composites for various industrial applications. Mixing conductive particles with insulating polymers can modify its electrical properties. The most common conductive filler used is carbon black (CB). The CB/polymer composites have been studied for their Positive Temperature Coefficient (PTC) effect and gas vapour sensing applications [1-9].

Some electrically conductive polymer composites show PTC behavior during one temperature range followed by negative temperature coefficient (NTC) behavior during the next range. The change normally occurs at a well-defined switching temperature. The switching temperature may be defined as the temperature below which the composite exhibits PTC characteristics and above which the composite exhibits NTC characteristics. Providing that certain conditions are fulfilled, it has been demonstrated in several moderately high temperature applications that mixing polymers with some types of conductive filler such as CB can produce a composition with a temporary electrical conductivity [1]. This is attributed to the forming of a chain of filler particles (network) that are close enough for an electrical current to flow at certain temperatures and generate heat. This phenomenon is known as percolation. The point at which the network is formed is called the percolation point/limit. Studies have shown that the electrical property of the composite is a direct function of the morphology and location of the CB in the polymer [8-11].

Different methods of preparing CB/polymer composites have been employed to improve properties of the material. Some used physical mixing of CB and the polymer matrix and the composite powders are cross-linked [7,8, 10]. Others used in-situ polymerization in the presence of CB [2]. They are also prepared by melt-mixing or solution mixing where CB is mixed with a polymer matrix dissolved in a solvent [3, 9]. For most of these methods, it is difficult to attain good dispersion of the CB into the polymer matrix which affects the percolation limit of the composite. This is due to the strong agglomeration tendency of the CB, limited shear force of the mixer and the high viscosity of the polymer solution.

Previous investigations have shown that ultrasonic treatment results in the formation of homogeneous mixtures of both powders [11] and liquids [12]. In this paper, the effect of ultrasonic mixing of CB and polymer powders on the percolation limit of their composites is presented. The composites prepared by this method are tested for their effectiveness for organic gas sensing applications. The main purpose of this composite is two fold. First it is intended to develop an organic gas detector. Once this detector is produced, calibration will be conducted to produce a gas sensor which is capable of measuring the gas concentration in an environment.

2   Experimental Procedure

Carbon black (CB) powder from Denka Chemicals and poly(methyl methacrylate) (PMMA) beads from ACROS Chemicals were used to prepare the conductive polymer composites. Different ratio of CB and PMMA powders were subjected to ultrasonic mixing using a VibraCell (Sonic and Materials Inc.) ultrasonic mixer. The homogeneous powder mixture was then dissolved in acrylonitrile solution.

To produce a gas-detector/sensor, a pasty composite solution of CB/PMMA was uniformly coated onto glass strips fitted with two parallel coils of copper wires serving as electrodes.

The main intention of this device is to be used to detect the presence of gas as well as its concentration. To calibrate this, the electrical resistance of the composite has to be determined under various organic gases and at different concentrations.

The electrical resistance was recorded using a Hewlett Packard 34401A digital multimeter in the four-wire mode. The change in the electrical resistance of the composites when exposed to organic vapours was determined. Vapours of volatile liquids were generated using a closed glass chamber. A given volume of liquid was injected into the chamber, which had a known volume. The molar vapour concentration c_{vapor} (ppm) was calculated using the sample density d (g/L), molar mass MM (g/mol) and volume V_{sample} (L), as well as the chamber volume $V_{chamber}$ and the molar volume of air (22.4 L/mol):

$$c_{vapor} = [(d \times V_{sample})/MM]/[V_{chamber}/22.4] \qquad (1)$$

When the electrical resistance of the composite approached its equilibrium value, the composite sensor was removed from the closed vessel and the change in electrical resistance in air was recorded.

3   Results and Discussion

The measured resistivity of the CB/PMMA composites is shown in figure 1. This figure shows the variation of the resistivity with % CB by weight in the composites.
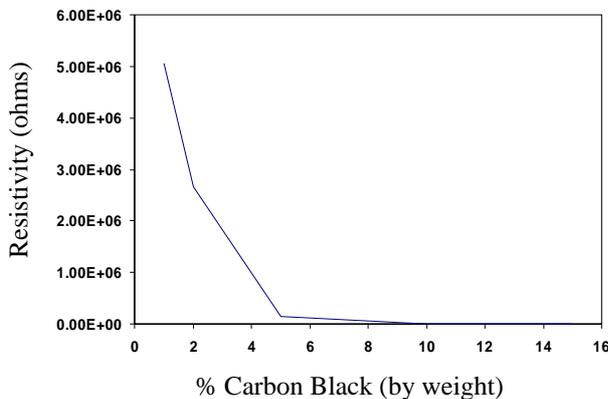

Figure 1: Resistivity of CB/Carbon Black composite vs. % Carbon Black.

It is indicated that as the % CB increases, the resistivity of the composite decreases. The percolation point is located between 2 % to 5 % CB. This value is lower than the values reported in other CB/PMMA composites which were found to display percolation of more than 10 % CB [9].

Figure 2 shows the change of resistivity of the composite sensor when exposed to acetone vapour.

The dashed line defines the vapour absorption and desorption zone. This gives a typical dependence of composite resistance on time when exposed to gas vapour. The composite sensor used has 10% CB content. Composite resistance increases during organic vapour absorption and returns to the initial value when vapour desorbs completely in air.
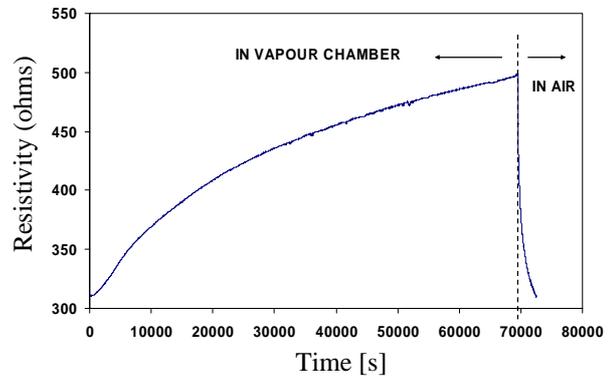

Figure 2: Typical electrical resistance response of CB/PMMA composite to acetone vapour (120.6 ppt).

The relative electrical resistance response is defined as:

$$(R_t - R_o)/R_o \qquad (2)$$

where R_o is the initial resistance of the composite and R_t the transient resistance upon exposure to the gas vapour.

The relative electrical response of CB/PMMA composite sensor when exposed to acetone vapour is given in figure 3. The change of electrical resistance in the sensor was monitored when the sensing element was exposed to gases. It is clearly indicated that the relative resistivity increases with the time of exposure to the vapour. Repeating the same tests on other gases will produce a trend identical to figure 3. This implies that if several tests are conducted on various gases, one can establish a trend which will be used as a scale for the sensor.

Different vapours will result in different dependencies of electrical response on vapour concentration. This may then be used to quantify and distinguish different vapour species. Currently the authors are obtaining some more experimental results which we anticipate to put in the final version of the paper.

The absorption and desorption kinetics of the CB/PMMA composite in acetone vapour were modelled using the transient response data shown in Figure 2. The model for the transient response is assumed to be given by a sum of exponentials such as:

214

$$R_t = R_\infty + Ae^{-\alpha t} + Be^{-\beta t} + Ce^{-\gamma t} + \ldots \ldots \quad (3)$$

The transient response model for the adsorption stage is estimated by the equation:

$$R_t = 518 - 237.68e^{-0.00003304t} + 30.25e^{-0.000070t} \quad (4)$$

This gives a reasonable agreement with the transient response data obtained from the experiments as shown in Figure 3.

For the desorption stage, the response model is given by:

$$R_t = 309.396 + 140.36e^{-0.00036514t} + 49e^{-0.002t} \quad (5)$$

Again, very good agreement between the response model and the experimental data is observed for the desorption stage as shown in Figure 4. It is also apparent that the time response in the desorption stage is much faster than in the adsorption stage. For the slowest pole the desorption stage is faster than the adsorption stage by a factor of 10.
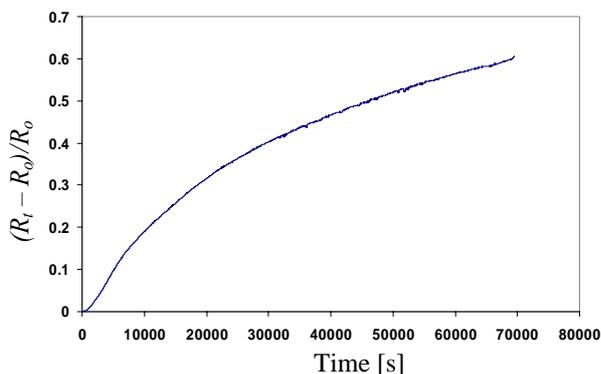
Figure 3: Time dependencies of relative electrical resistance response of CB/PMMA composite in acetone vapours (120.6 ppt).
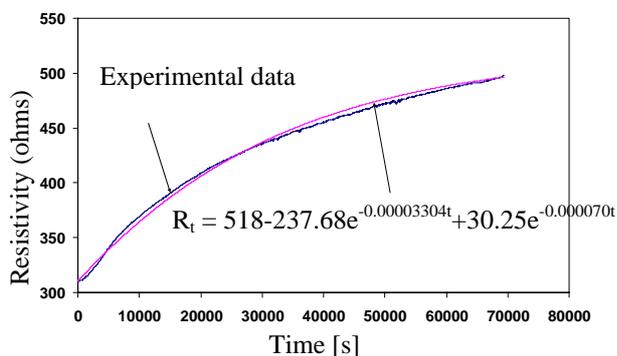
Figure 4: Transient resistance response model of CB/PMMA composite in acetone vapours (120.6 ppt)-(adsorption stage).
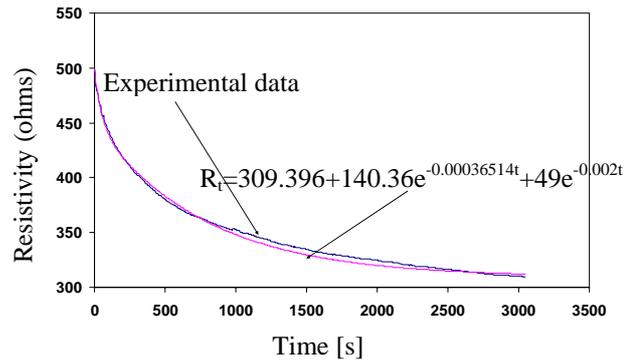
Figure 4: Transient resistance response model of CB/PMMA composite in acetone vapours (120.6 ppt)-(desorption stage).

4   Conclusion

The results have shown that CB/PMMA composite has potential for detecting gas vapours. The use of ultrasonic mixing to prepare the composite has improved the homogeneity of the composite mixture and results in lower percolation rate for CB. The CB/PMMA composites should be tested with various types of gas vapours at different concentration and obtain a kinetic model of the gas detection system.

5   References

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