Response of Poly(vinyl acetate)\Carbon Black Composites to Ethanol Vapour and Temperature

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Abstract - The effect of ethanol vapour and temperature was investigated on gas sensors fabricated from poly(vinyl acetate)\carbon black composites based around a predetermined percolation threshold. Samples with 8% carbon black loading displayed the best response to the ethanol vapour. Typical response and recovery times of 140s and 45s respectively were recorded. In addition, bridge structures were fabricated, where all four resistive elements were prepared from the same composite material and in which a novel passivation process was employed. It was observed that these bridge structures were significantly less affected by variations in temperature in comparison to the single sensor structures.

I. INTRODUCTION

Conducting polymer composites, consisting of an insulating polymer phase and a conducting phase, often carbon black, have proven successful as gas sensitive resistors [1]. The permeation of gasses into these polymer composites leads to expansion of the material which results in a decrease in the conductivity [2]. The conductivity of these materials and their response to compression or expansion can be explained by percolation theory [3]. Theoretically, when the volume fraction of a conductive filler reaches the percolation threshold, the first continuous conducting filament is completed through the polymer, resulting in a sharp fall in the resistivity of the composite [4]. Volume changes in compositions based around the percolation threshold, have been found to have large effects on the conductivity, where compression leads to increased conductivity and, conversely, expansion leads to decreased conductivity [5].

In this paper the effects of ethanol vapour on poly(vinyl acetate)\carbon black composites, based around a derived percolation threshold, have been investigated. In addition, to address two of the main disadvantages of conducting polymer sensors, namely, (i) a large temperature coefficient of resistance and (ii) significant batch-to-batch baseline resistance variation, a bridge structure was constructed. This bridge had all four resistive elements prepared from the same composite material, in order to reduce the effects of operating temperature and batch-to-batch variability on the sensor baseline signal.

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II. EXPERIMENTAL

A. Polymer composite preparation

Polymer composites were prepared from poly(vinyl acetate) (PVAc) filled with percentages of carbon black (CB), ranging from 4% to 30% w/w. The CB used in preparing the PVAc\CB composites was black pearls 2000 (Cabot Corporation[1]). The PVAc and tetrahydrofuran were supplied by Sigma-Aldrich[2].

The various mixtures of PVAc\CB were added to 20ml of tetrahydrofuran and each composition was shear mixed for 15 minutes prior to deposition to attain a homogenous suspension.

B. Sensor fabrication

The sensors were fabricated by depositing the composite materials onto PCBs – containing copper electrode patterns – using a microlitre pipette. The average volume of composite deposited was 6μL. For the bridge-type sensors, a bridge structure was constructed with all four resistive elements prepared from the same composite material.

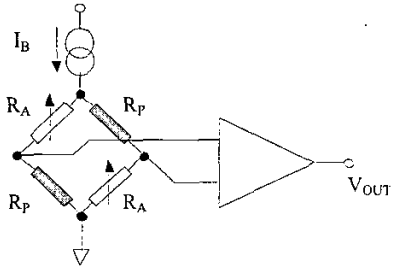

Fig. 1. The interface circuit and bridge sensor layout showing active (R_A) and passivated (R_P) sensor elements.

[1] Cabot Carbon Limited. Lees Lane, Stanlow, Ellesmere Port, South Wirral L65 4HT, England.
[2] Sigma-Aldrich Ireland Limited, Dublin, Ireland.

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Two of the resistive elements were then passivated against the analyte vapour, by covering them with epoxy-coated paper and subsequently sealing this over with an adhesive membrane. No change in resistance was observed during this novel passivation process. The interface circuitry used to interrogate the bridges is shown in Fig. 1. The circuitry drives the bridge with a constant current (I_B) of 104μA, the output of the bridge is fed into an instrumentation amplifier, which has a gain set to 100.

For the temperature tests, the set-up of Fig. 1 was again used to interrogate the bridge sensors (but with the amplifier set to unity gain), while a similar circuit arrangement, shown in Fig. 2, was used to interrogate the single sensors.

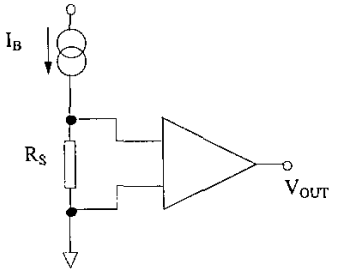

Fig. 2. The interface circuit arrangement used to interrogate the 6% CB filled PVAc single sensor (R_S). The bias current (I_B) was again set at 104μA. The amplifier is set to unity gain.

C. Sensor testing apparatus

The sensors were tested using a custom designed injection test chamber (volume 2.4L). A schematic representation of the test chamber is shown in Fig. 3. A specific amount of liquid ethanol was injected into the chamber via a syringe to give the desired concentration of ethanol vapour. The base of the chamber was heated; this (i) evaporated the injected liquid ethanol, (ii) prevented condensation of the vapour on the sides of the flask and (iii) allowed the temperature inside the chamber to be held constant.

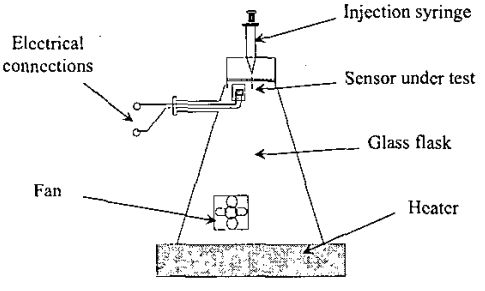

Fig. 3. Schematic diagram of the test chamber used to measure the ethanol vapour responses.

III. Results and Discussion

A. Determination of percolation curves

The percolation curve of a PVAc\CB composite represents the changes in the resistivity of the composite with respect to varying volume fractions of CB.

To determine the percolation curve for PVAc\CB , 6μL drops of the composites containing varying fractions of CB (4% - 30% w/w) were deposited onto PCBs containing parallel plate copper electrodes. The resistance of the deposited composites was measured using a multimeter (Thurlby Thandar 1705) and the thickness of the composite measured using a profilometer (Sloan Dektak 900051). The resistivity ρ of each sample was then determined by Eq. 1:

$$\rho = \left(\frac{R.t.b}{l} \right) \tag{1}$$

where R is the resistance of the composite, t is the thickness of the composite, b is the width of the copper electrodes and l is the distance between the electrodes.

The graph of Fig. 4 shows the determined percolation curve for PVAc\CB composite.

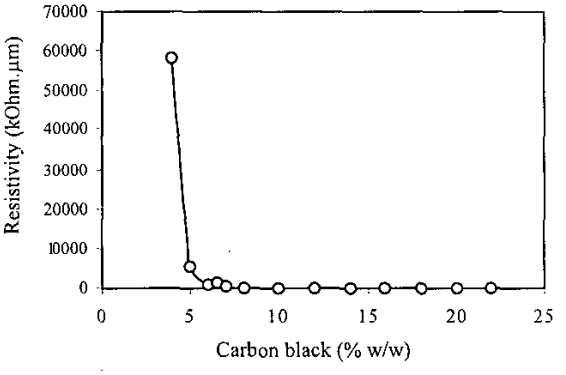

Fig. 4. Resistivity vs. carbon content for PVAc\CB composites.

From the graph of Fig. 4, it is evident that the percolation threshold occurs at approximately 6% CB loading.

B. Sensor responses to ethanol vapour

Exposure of the sensor to a vapour causes swelling of the polymer [1]. This expansion of the polymer matrix decreases the effective volume fraction of the conducting phase, which causes an increase in the electrical resistivity. This resistivity change is larger for samples where the volume fraction of the conducting phase is close to the

percolation threshold [4]. For this reason, sensors were fabricated from the polymer compositions with 6%, 8% and 10% CB. The results for these sensors when exposed to ethanol vapour in the concentration range 0–21,200ppm are shown in Fig. 5. For the results of Fig. 5, the percentage relative change in resistance (ΔR/R %), defined in Eq. 2, is chosen as the parameter to represent sensor response.

$$\Delta R/R\,\% = \left(\frac{R_{vapour} - R_0}{R_0}\right) \times 100 \qquad (2)$$

where R_{vapour} is the sensor resistance if the sensor is exposed to a certain concentration of ethanol vapour and R_0 is the sensor baseline resistance.

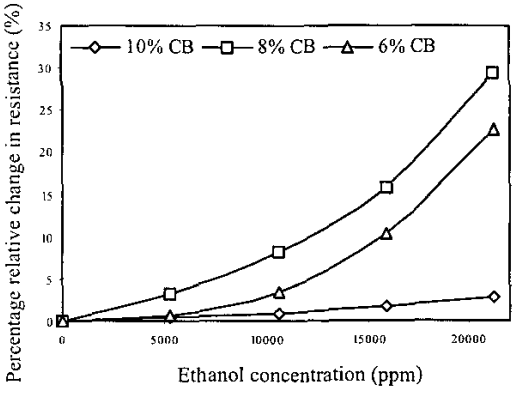

Fig. 5. Responses to ethanol vapour of three PVAc sensors filled with 6%, 8% and 10% CB – at a temperature of 30°C and a relative humidity of 43.2%.

It can be seen from Fig. 5 that the sensors display a significant response to the ethanol vapours, which can be accurately modelled by a second order polynomial. It can also be seen that the sensor with the 8% CB loading outperforms both the other samples.

C. Response and recovery times

The response time is defined as the time it takes to reach 90% of the maximum saturated conductance value following a step change in gas concentration at the sensor, while the recovery time is the time it takes to return to 10% of the saturated value [6]. Fig. 6 shows the typical transient response curve for the sensors. In determining the response and recovery times in this case, one of the 6% CB filled samples was exposed to a 0–5,400ppm step change in ethanol concentration (at t=0s), subsequently (at t=240s) the ethanol vapour was flushed from the chamber. The response and recovery times ($t_{0\text{-}90\%}$) are calculated to be 140s and 45s respectively.

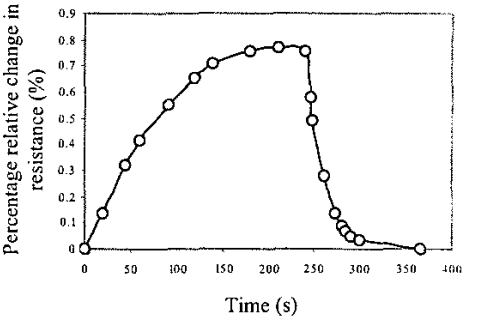

Fig. 6. Typical response and recovery characteristics of the sensors, following a step increase (0–5,400ppm) in ethanol concentration and subsequent removal of ethanol vapour – at a temperature of 26°C and relative humidity of 42.9%.

D. Bridge-type sensors

The two best performing composites determined from the earlier testing, i.e. the 6% and 8% CB filled samples, were used to create the bridge sensors. The results for these bridge sensors when exposed to ethanol vapour in the concentration range 0–12,250ppm are shown in Fig. 7.

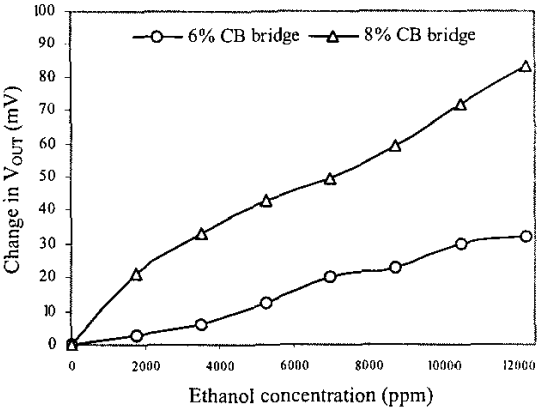

Fig. 7. Response of 6% and 8% CB filled PVAc bridge sensors to ethanol vapour at a temperature of 30°C and a relative humidity of 43.5%. The instrumentation amplifier gain is set at 100.

It can be seen from Fig. 7 that the bridge configurations display an excellent response to ethanol vapour and their response is relatively linear in the range tested. Also, as expected from earlier results, it is clear that the bridge based on the 8% CB filled PVAc composite outperforms the 6% CB loaded sample.

The effect of temperature on the PVAc - 8% CB single sensors and bridge sensors was also investigated. The sensor temperature was varied in the range 5– 40°C.

The results of the temperature tests are shown in Fig. 8 and it can be seen that the bridge structures are significantly less affected by temperature variation in comparison to the single sensor structures.

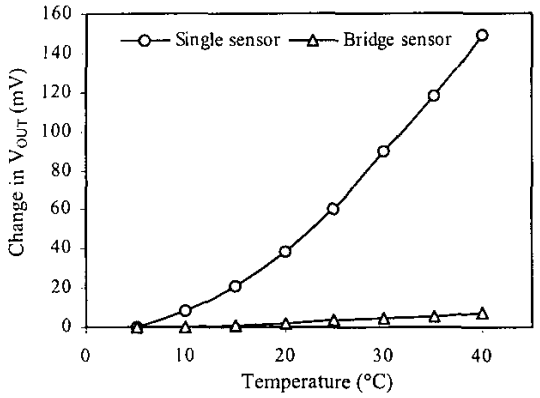

Fig. 8. Effects of temperature on the 8% CB filled PVAc single and bridge sensor structures. Both structures were driven with a constant current of 104μA, with the amplifier set to unity gain.

In the variation of temperature from 5°C to 40°C, the single sensor output voltage was seen to change by 149mV, while in the same temperature range, the bridge sensor output voltage was seen to change by a mere 7.11mV – thus demonstrating the substantial temperature compensation advantages of the bridge structure. Moreover, utilisation of the same composite in creating all the resistive elements minimised bridge offset error due to the elimination of batch-to-batch process variability.

III. Conclusion

In this study the percolation threshold for a PVAc\CB composite was found to lie at approximately 6% CB loading. Effects of ethanol vapour on sensors fabricated from compositions close to this percolation threshold (6%, 8% and 10% CB filled) were then investigated. The sensors with 8% CB loading displayed the best response to the ethanol vapour. The devices also displayed good response and recovery times of 140s and 45s respectively.

Moreover, experiments on bridge sensor structures, in which all four resistive elements were prepared from the same composite and where a novel passivation process was employed, proved to obviate two of the main disadvantages of conducting polymer composite sensors, namely, (i) the large temperature coefficient of resistance and (ii) significant batch-to-batch variation.

Acknowledgement

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