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Sensing properties of the CB–PCV composites for chlorinated hydrocarbon vapours

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The conductivity measurements of carbon black (CB)–polyvinyl chloride (PCV) composite in a tetrachloride (CCl_4), trichloromethane (chloroform, $CHCl_3$) or methylene chloride (CH_2Cl_2) vapour ambient have been performed. The composite contains 20% Chezacarb K2 carbon black and was prepared as a plastic strip. Based on the $\sigma = f(t)$ dependence, three methods to determine the vapour concentration, *c*, are presented. The investigations could allow one to construct a CCl_4 and $CHCl_3$ vapour detector.

1. Introduction

A great many organic materials are sensitive to the gas or vapour atmosphere that surrounds them [1–6]. In the case of composites such as polyvinyl chloride (PVC) with carbon black (CB) investigated by us, the gas absorption is followed by swelling of the polymer matrix.

In the present work we studied electrical properties of the composite CB–PCV placed in atmospheres of carbon tetrachloride (CCl_4), trichloromethane (chloroform, $CHCl_3$) or methylene chloride (CH_2Cl_2) to explore the possibilities of using it in a gas-sensing device. As is commonly known, all these gases are harmful and dangerous to health.

2. Materials

All of the chlorocompounds employed in our research were analytically pure. The CB–PCV composite used contains Chezacarb K2 carbon black (Czecho-Slovakia), and was in the shape of a plastic strip. Its basic properties are shown in Table I.

3. Experimental procedure

During the investigations two rectangular samples were used: 8.00×10^{-3} m $\times$ 1.90×10^{-3} m and 9.00×10^{-3} m $\times$ 4.46×10^{-3} m with a thickness of 0.14×10^{-3} m in both cases.

The sample was assembled between copper electrodes and contacted with silver paint (in this manner a sandwich-type arrangement was set up), and then put into the teflon casing of the measuring cell. The electrical measurements were made by the standard d.c. method using a Keithley 197A Multimeter, controlled by an IBM PC, in the following order.

1. The measuring cell was heated to the measurement temperature.
2. The chlorocompound was injected into the cell.
3. The kinetics of sample resistance changes were monitored in two steps: (a) with a duration of 16 min with measurements taken every 10 s; (b) with a duration of 90 min with readings every 60 s.
4. The chlorocompound vapour was sucked out.

The measurements were repeated for different temperatures ($T = 293.2$, 323.2 K) while the vapour concentration, *c* was held constant, and for different concentrations ($c = 0.039$, 0.36 g dm^{-3} for CCl_4, 0.037, 0.34 g dm^{-3} for $CHCl_3$, and 0.033, 0.30 g dm^{-3} for CH_2Cl_2) while *T* was held constant. On the whole, 216 measuring series were performed.

4. Discussion

For all the temperatures studied, similar shapes of electrical resistivity versus time dependence curves (see Fig. 1) were observed. We propose the following interpretation of the resistivity changes with time. In Part a, evaporation of liquid CCl_4, $CHCl_3$ or CH_2Cl_2: the changes in resistance are slow; in Part b, the vapour is absorbed into the CB–PCV composite. CCl_4, $CHCl_3$ and CH_2Cl_2 cause swelling of PCV in the sample, so the volumetric concentration of the carbon black decreases: it causes a decrease in conductivity of the sample (depending on the vapour concentration, a few or many of the conducting paths formed between the carbon black particles are broken): the resistance

TABLE I Basic properties of CB–PCV [7]

Concentration (%)		Surface resistance (Ω)	Tensile strength (MPa)	Tear extensibility (%)
CB	Plasticizer			
20	40	150	6.5	68

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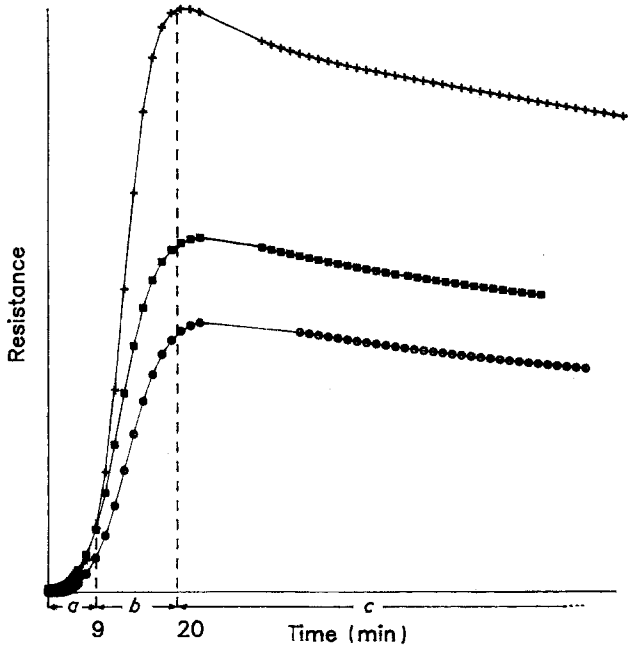

Figure 1 The kinetics of changes of resistance, an example for c = constant and different temperatures. (----) T_1, (□) T_2, (○) T_3; $T_3 > T_2 > T_1$, c = constant.

reaches the largest value in a short time; in Part c, the stabilization of sample resistivity occurs.

Measurements were discontinued with CH_2Cl_2 ambient, because the differences in resistance between the consecutive measurements were too small. For CCl_4 and $CHCl_3$ the changes were from one to three orders of magnitude and the largest for temperatures around room temperature.

Analysing Fig. 1, we can see, that σ increases with temperature, suggesting a semiconducting character of the samples. For c = constant, the following equation describing the electrical conductivity, σ, dependence on temperature, T, was fulfilled

$$\sigma = \sigma_0 \exp\left(-\frac{E_t}{kT}\right) \qquad (1)$$

where E_t is the activation energy, k Boltzmann's constant, and T the thermodynamic temperature.

The data of the kinetics of resistance changes (see Fig. 1) are used to obtain the set of electrical parameters (σ, E_t, and σ_0).

Fig. 2 shows the thermal activation energy, E_t, dependence on the CCl_4 and $CHCl_3$ concentrations for different exposure times from Part c. E_t values (independent of the exposure time) for the same concentration of vapour are nearly equal (within the accuracy of measurements of 9.0%; in Fig. 2 the mean E_t values are given). For CCl_4 concentrations ranging from 0.039–0.24 g dm^{-3}, E_t increases, and for higher vapour concentration it decreases; we observe similar behaviour for $CHCl_3$ (E_t reaches maximum for $c = 0.22$ g dm^{-3}).

It may be expected that a decrease in E_t will correspond to an increase in electrical conductivity. However, for concentrations higher than 0.24 g dm^{-3} for CCl_4 and 0.22 g dm^{-3} for $CHCl_3$, the opposite behaviour is observed; this could be connected with a change in the charge transport mechanism in the material investigated.

Fig. 3 shows $\log \sigma = f(c)$ dependences for different exposure times and two temperatures. We found that an increase in temperature follows that of the diffusion of vapour into the sample. The fast diffusion causes rapid swelling of the composite. Indeed, a decrease in the minimum value of conductivity with increase of vapour concentration was found, but even for the largest concentrations used, the $\log \sigma = f(c)$ curve did not reach saturation.

Fig. 4 shows the changes of σ for different gas concentrations (cf. Fig. 1); in all cases the time needed to reach the minimum conductivity value was about 20 min. Hence a time longer than 20 min is needed for an unequivocal determination of the vapour concentration, c, by measuring of one σ value of the CB–PCV composite.

In looking for another method of determining the CCl_4 and $CHCl_3$ concentrations, we have found that

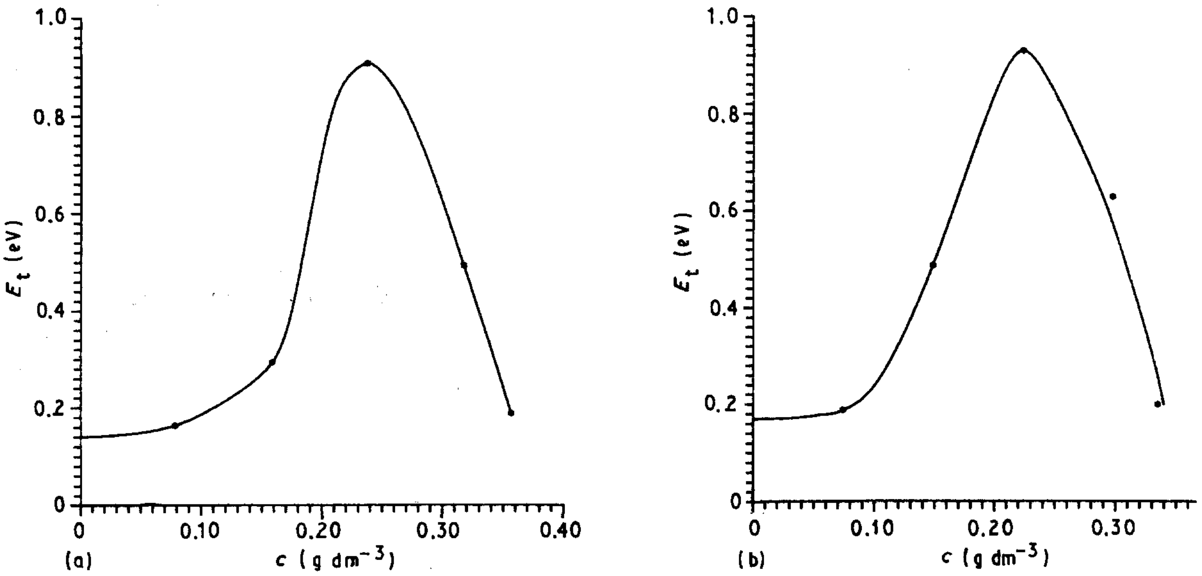

Figure 2 The dependence of thermal activation energy, E_t (mean values for different exposure times from Part c) on (a) CCl_4 and (b) $CHCl_3$ concentrations.

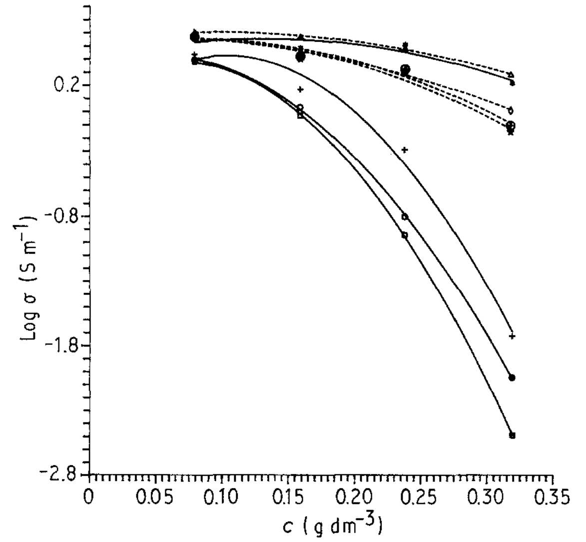

Figure 3 An example of the dependence of CCl_4 of log $\sigma = f(c)$ on different exposure times at (✱, +, □, ○) $T_1 = 294.0$ K and (△, ◇, ☆, ⊕) $T_2 = 318.0$ K. (✱, △) $t_1 = 3$ min, (+, ◇) $t_2 = 15$ min, (□, ☆) $t_3 = 30$ min, (○, ⊕) $t_4 = 80$ min.

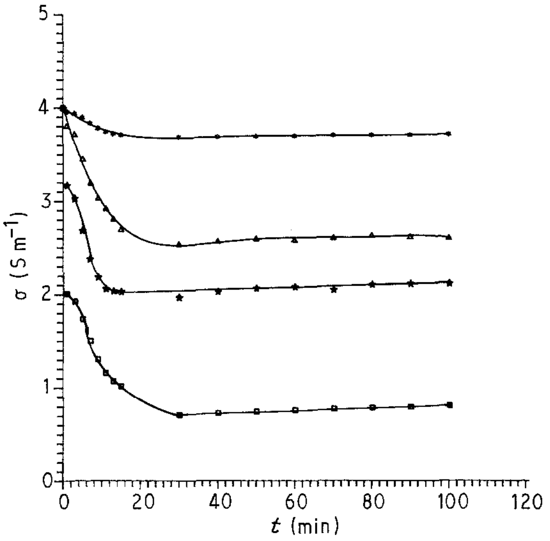

Figure 4 An example of the dependence of electrical conductivity on time, for different concentrations, c, of CCl_4 and $T = 318.0$ K. (✱) $c_1 = 0.079$ g dm^{-3}, (△) $c_2 = 0.16$ g dm^{-3}, (☆) $c_3 = 0.24$ g dm^{-3}, (□) $c_4 = 0.32$ g dm^{-3}.

it is possible to obtain earlier (than 20 min) information on the value of vapour concentration by analysing the time dependences of conductivity around room temperature, $\sigma = \sigma(t)$ (here the largest changes in σ are observed). At first we compared the differences, $\Delta\sigma$, between the sample conductivity value, $\sigma(10)$, after 10 min exposure in the vapour, and its conductivity in fresh air, $\sigma(0)$, as a function of the gas vapour concentration ($\Delta\sigma = f(c)$) for $T_1 = 293.5$ K, $T_2 = 295.9$ K, and $T_3 = 298.4$ K. We found an exponential equation ($\Delta\sigma = A\exp^{Bc}$) to give the best fit describing those dependences (see Table II).

Next, we ignored all measurements over 0.16 g dm^{-3} for CCl_4 and 0.15 g dm^{-3} for $CHCl_3$ (these concentrations are very large, and much higher than the limits set up by the Health Authorities). This time all the dependences were approximately linear ($\Delta\sigma = a_1c + b_1$) (Table II).

Another method developed for the determination of c requires a somewhat shorter time for the measurement. Here the linear approximation of Part b (see Fig. 1) was made beginning at 9 min, both for CCl_4 and $CHCl_3$ (but it is possible to start earlier, e.g. after 5 min for $CHCl_3$ vapour). Here about 20 readings of sample resistance in, for example, 1 s steps, were taken. Then the slope, a', of the conductivity–time dependence was calculated. The value of a' depended linearly on the chlorocompound concentration. For the relation $a' = a_2c + b_2$, higher values of correlation coefficient, r (see Figs 5 and 6 and Table III), have been obtained, than those in Table II and the significance level for the Student's test is equal to 0.999 in all cases. Figs 5 and 6 show that the $a' = a_2c + b_2$ dependences are influenced by temperature (the higher the temperature the lower the slope a).

The last dependences (see Fig. 5 for CCl_4 and Fig. 6 for $CHCl_3$) can be a basis for constructing a device to detect $CHCl_3$ and CCl_4 vapour concentrations.

5. Conclusions

The composite CB–PCV film is a good sensing material for constructing a detector of CCl_4 and $CHCl_3$ vapours. The best operating conditions are around room temperature (the largest changes in sample resistance) so that heating the sample is not required. It is important that the resistance is not high and could be easily measured.

Three methods by which to determine $CHCl_3$ and CCl_4 are presented. The essential one is that examining a change in a decrease of sample conductivity (slope) on time of exposure. This slope (after 5 min exposure to $CHCl_3$ and 9 min to CCl_4) is linearly dependent on the vapour concentration.

In the second method, we have found that the difference $\Delta\sigma = \sigma(10) - \sigma(0)$ is dependent linearly on c. However, here the larger random error of the

TABLE II The coefficients A, B of the equation $\Delta\sigma = A\exp^{Bc}$ for a large interval of concentration, and slope, a_1, intercept b_1, and correlation coefficients r of $\Delta\sigma = a_1c + b_1$ dependence for the initial concentration interval (up to 0.16 g dm^{-3} for CCl_4 and 0.15 g dm^{-3} for $CHCl_3$)

Vapour	T (K)	A ($\times 10^{-2}$)	B	r	a_1	b_1	r
CCl_4	293.5	5.6	7.1	0.840	1.84	-1.7×10^{-2}	0.717
	295.9	4.5	14.9	0.888	4.95	−0.254	0.988
	298.4	1.4	24.8	0.982	5.10	−0.262	0.968
$CHCl_3$	293.5	6.0	14.5	0.856	6.30	−0.389	0.926
	295.9	3.9	16.4	0.884	7.65	−0.503	0.950
	298.4	1.9	20.6	0.915	9.41	−0.680	0.876

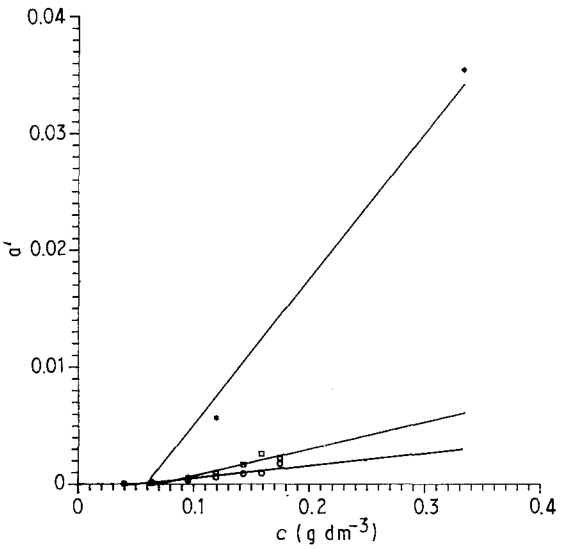

Figure 5 The dependence, a', as a function of the CCl_4 vapour concentration, c, for (∗) $T_1 = 293.5$ K, (□) $T_2 = 295.9$ K and (○) $T_3 = 298.4$ K.

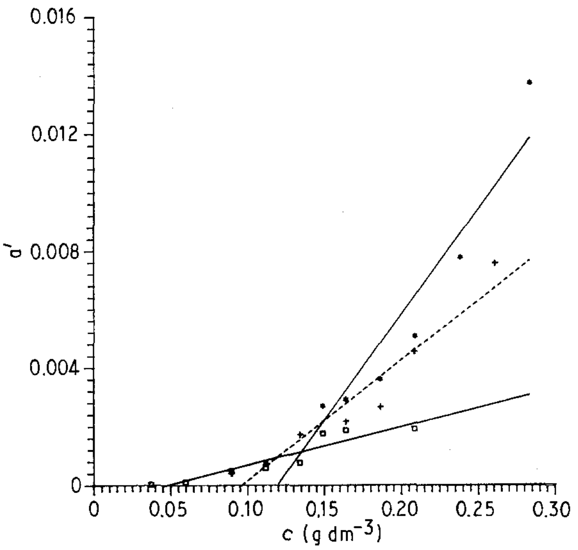

Figure 6 The dependence, a', as a function of the $CHCl_3$ vapour concentration, c, for (∗) $T_1 = 293.5$ K, (+) $T_2 = 295.9$ K and (□) $T_3 = 298.4$ K.

TABLE III Slope a_2, intercept b_2, correlation r and t (of Student's test) coefficients of the $a' = a_2c + b_2$ dependence

Vapour	T (K)	a_2 ($\times 10^{-2}$)	b_2 ($\times 10^{-3}$)	r	t
CCl_4	293.5	12.4	−7.3	0.983	0.999
	295.9	2.3	−1.6	0.951	0.999
	298.4	1.1	−0.5	0.926	0.999
$CHCl_3$	293.5	7.2	−8.6	0.956	0.999
	295.9	4.1	−3.9	0.959	0.999
	298.4	1.3	−6.0	0.932	0.999

measurements leads to less precise determination of the vapour concentration.

The third method requires a duration of 20 min to reach the stabilized σ value.

The same sample could be exposed to the vapours many times (after describing them by heating the sample).

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