Electrical Resistance Response of Poly(ethylene Oxide)-Based Conductive Composites to Organic Vapors: Effect of Filler Content, Vapor Species, and Temperature

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ABSTRACT: In this work conductive composites consisting of carbon black (CB) and poly(ethylene oxide) were prepared by solution mixing. The composites' resistance drastically changes in organic vapors so that the composites can be used as candidates for gas-sensing materials. Owing to the different conduction mechanisms and solvent/composites interactions, the electrical response behaviors of the composites exhibit specific dependences on CB content and environmental temperature, which were only reported previously in a few instances. In addition, the rate of response was also correlated with solvent polarity, solubility, etc. The findings would help to understand the micromechanism of response of the composites and to improve the sensing performance as well. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1517–1523, 2005

Key words: composites; sensors; swelling

INTRODUCTION

Owing to the wide application potentials in electromagnetic interference shielding, electrostatic discharge, and thermosensitive devices, conductive polymer composites consisting of intrinsically insulating polymer and conducting fillers (like carbon black, metal power, etc.) have been intensively studied.[1] Recently, gas sensors or chemically sensitive materials made from conductive polymer composites received significant attention for use in detecting, quantifying, and discriminating various organic vapors.[2–4] The working principle is based on the drastic variation in electrical resistance of the composites in the environment of odor.

Tsubokawa and coworkers[5–11] reported that a series of semicrystalline polymer-grafted carbon black/semicrystalline polymer composites exhibit great electrical resistance responses toward certain organic vapors. Narkis and colleagues[12,13] employed immiscible polymer blends as the matrices of conductive composites for manufacturing solvent sensors and indicated that the systems are rather sensitive to temperature, swelling, and pressure due to the effect of double-percolation compared with the composites using a single polymer as matrix. Zhang and coworkers synthesized amorphous polymer-based composites by polymerization filling.[14–19] Owing to the intimate interfacial contacts, the resultant composites are provided with low percolation threshold, good processability, and reproducible sensitivity against organic vapors.

So far, there are two explanations accounting for the organic vapor induced change in electrical resistance of composites according to percolation theory, i.e., swelling model,[20] and crystallites dissolution model.[5–11] In the former, swelling of the polymeric matrix in a composite due to absorption of solvent takes responsibility for the changes of electric resistance because of the expanded interfiller gaps. However, it is challenged by the counterexample that the composites with conducting fillers lower than the percolation threshold exhibit resistance reduction upon exposure to certain solvent vapors.[21] According to the mechanism of crystallites dissolution, change in the crystalline structure or flow of the dissolved crystal-

line phases is the main reason for the variation in electric resistance. Evidently it does not work in the case of amorphous composites sensors.[14–16] For the time being, therefore, continuous efforts should still be made to explore the mechanisms of the gas response behavior and ways to improve the sensitivity as well.

In this paper, carbon black (CB) filled poly(ethylene oxide) (PEO) composites with different carbon black contents are prepared by solution-mixing method. Their electrical resistance responses against chlorinated hydrocarbon solvent vapors of CH_2Cl_2, $CHCl_3$, and CCl_4 at various temperatures are investigated. These solvents are selected because their similar molecular structures but different chemical features would facilitate a systematic study. By purposely changing the composites compositions and testing conditions, it is hoped that the mechanisms involved in the gas sensing behavior and sensitivity would be reasonably revealed.

EXPERIMENTAL

PEO (number-average molecular weight = 7.7×10^5) was purchased from Fluka AG without further purification and vacuum dried at 60 °C for 24 h before use. Conductive carbon black (XC-72), supplied by Cabot, with a N_2 specific surface area of about 254 m^2/g and average primary particle diameter of 50–70 nm, was vacuum dried at 110 °C for 48 h before use. The chlorinated hydrocarbon solvents, CH_2Cl_2, $CHCl_3$, and CCl_4, which act as solvent vapor sources in this work, are analytical reagents and used as received.

CB/PEO composites were prepared by solution-mixing as follows. The 2% (w/v) solution of pre-weighed PEO in chloroform was blended with CB particles. After 45 min of high-speed stirring, the suspension was cast onto an epoxy plate with comb-like electrodes. To remove the residual solvent in the blends, the cast films were laid in air at room temperature for 48 h and then vacuum desiccated at room temperature for an additional 48 h. Finally, the composites film 30–40 μm thick (determined by a thickness gauge with measurement accuracy of 1 μm) was available for subsequent characterization.

Electrical responses of the composites against saturated solvent vapors were detected through a digital multimeter by hanging the comb electrode coated with the composites film ($10 \times 20mm^2$) in a glass conical flask containing pure solvent at the bottom. The resistance recovery of the composites, which had been exposed to saturated solvent vapors, was measured by hanging the composites in a glass conical flask containing silica gel at the bottom. The response behavior is characterized by the time dependence of composites resistance variation R/R_0, where R is the transient resistance and R_0 is the original resistance in dry air. The corresponding maximum responsivity is
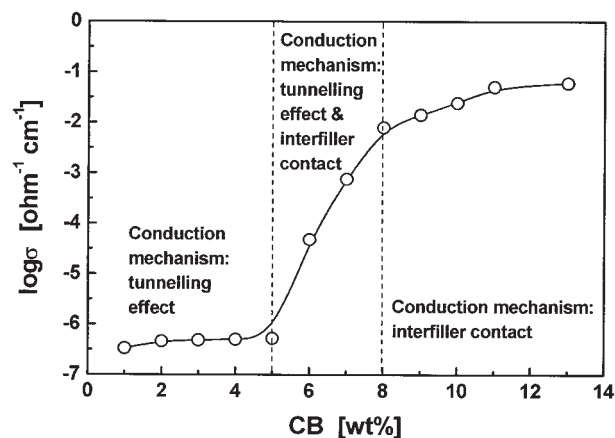

Figure 1 Electrical conductivity, σ, of CB/PEO composites as a function of CB content.

defined as R_{max}/R_0, where R_{max} is the maximum resistance in vapor. The above system was immersed in a water bath preset at a constant temperature, so that the vapor-sensing habits at different temperatures can be detected.

RESULTS AND DISCUSSION

The dependence of electrical conductivity of CB/PEO composites on CB content is shown in Figure 1. The percolation range lies in about 5–8 wt % of CB concentration. It is slightly lower than that of PEO-grafted CB/PEO composites,[8] because the dispersion of grafted CB in the latter composites is improved and the grafted polymer somewhat shields the conductive CB. According to the results shown in Figure 1, a series of composites with CB fraction ranging from 3 to 13 wt % was selected to test their responses against chlorinated hydrocarbon vapors. The resistivity of these composites covers several orders of magnitude from semiconductor to conductor, which would help to evaluate the response performance of the composites over a wide spectrum. Figure 2 illustrates the maximum responsivity of various composites in the saturated solvent vapors. In disagreement with the general prediction that the strongest response should be observed near the percolation threshold, the curves in Figure 2 peak at CB contents of 10 wt % for CH_2Cl_2 and $CHCl_3$ vapors and 9 wt % for CCl_4 vapor, which are all much higher than the percolation threshold of the composites (~6 wt %). This coincides with the results of other systems,[7,14–19] in which the maximum responsivity also appeared at CB contents far higher than the percolation thresholds. These results suggest that the vapor-induced electric resistance increase could not be simply explained by the percolation theory. The optimum CB content corresponding to the maximum responsivity is controlled by factors includ-
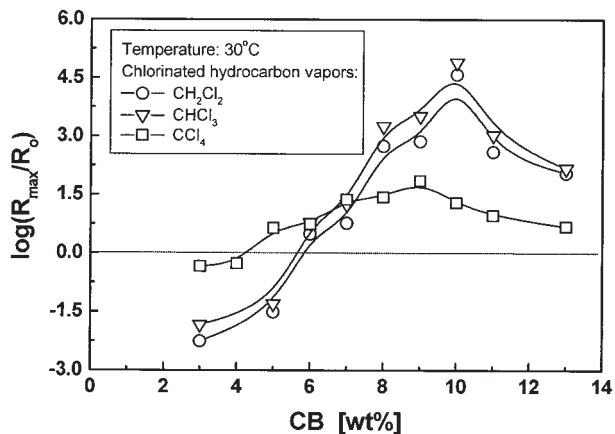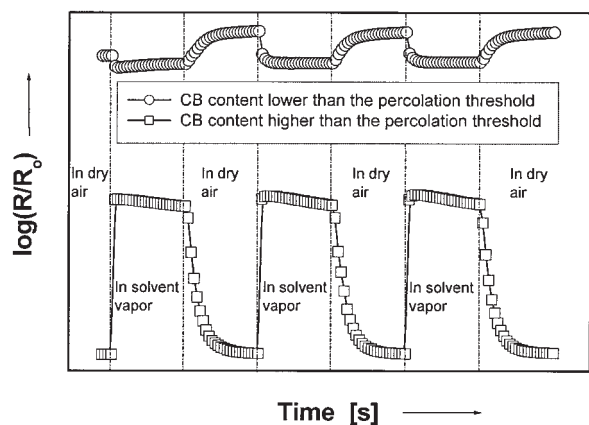
Figure 2 Maximum resistance variation of CB/PEO composites in response to chlorinated hydrocarbon vapors as a function of CB content.

ing the natures of polymer matrix and fillers, filler/matrix adhesion, solvent characteristics, and the interaction between the solvent and the composites.

It is interesting to see from Figure 2 that when the CB content is below or near the percolation threshold, the responses of the composites are characterized by negative vapor coefficient (NVC) phenomenon, presenting a striking contrast to the positive vapor coefficient (PVC) recorded in the composites with higher CB content. Figure 3 collects the typical response habits of the composites with different CB concentrations as a function of time, which clearly shows the opposite trends of resistance variation in solvent vapor and dry air. This means that different response mechanisms must be involved when CB content in the composites is changed. More detailed investigation in this aspect is needed.
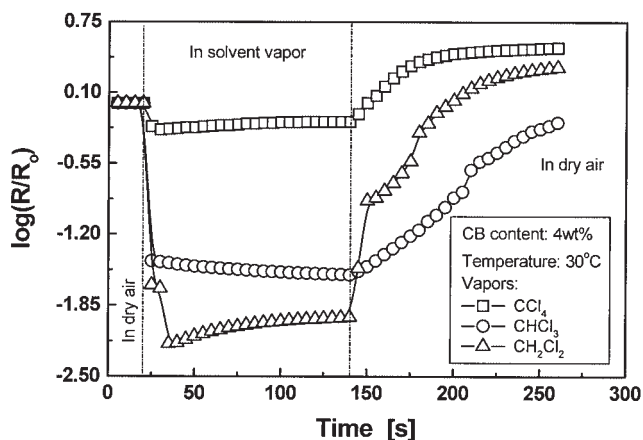
For the convenience of discussion, the composites are classified into three categories according to their

Figure 3 Typical response behaviors of CB/PEO composites with different CB contents in chlorinated hydrocarbon vapor. The dashed lines define the vapor absorption and desorption zones.
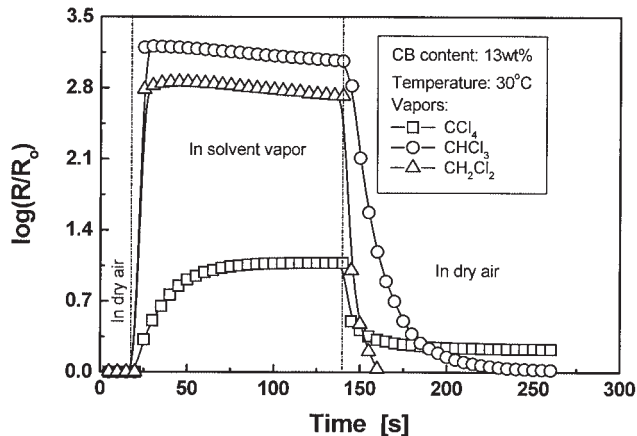

(a)

(b)

Figure 4 Resistance variation of CB/PEO composites in response to chlorinated hydrocarbon vapors. The dashed lines define the vapor absorption and desorption zones.

CB concentrations (Fig. 1), i.e., >8 wt % (above the percolation region), 5–8 wt % (within the percolation region), and <5 wt % (below the percolation region). Figure 4 illustrates the response behaviors of the composites with CB contents of 13 and 4 wt % in chlorinated hydrocarbon vapors at a constant temperature of 30 °C, respectively. For the composites with CB content higher than the percolation region (i.e., 13 wt %, see Fig. 4(a)), the electrical resistance drastically increases in the solvent vapors and then returns to the initial value when the sample is transferred to dry air. Such a PVC behavior has been widely found in many conductive composites sensors and is generally attributed to the matrix swelling induced disconnection of the conduction paths formed by the contacted conducting fillers. The lower maximum responsivity of the composites in CCl_4 vapor should be the result of the nonpolar nature of the solvent. Swelling of polar PEO matrix obeys the rule of "like dissolves like" (i.e., a solvent that has a similar polarity to the solute being
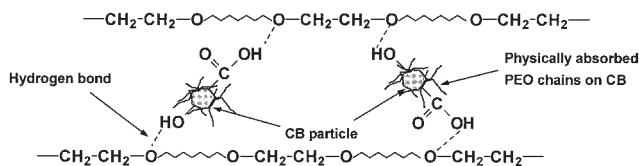
Figure 5 Schematic drawing showing the interfacial interactions in CB/PEO composites.

dissolved will usually dissolve the substance very well).

With respect to the composites with CB content lower than the percolation region, i.e., 4 wt % [Fig. 4(b)], however, the responses follow a trend just opposite to the above PVC manner. When the composites meet the solvent vapors, a great reduction in the resistance is observed. To the knowledge of the authors, only a few reports deal with this NVC behavior. In the case of PEO-grafted CB/PEO composites, for example, similar phenomena were recorded but there was no detailed explanation.[7]

A careful survey of Figures 2 and 4(b) indicates that the maximum resistance variations of the composites are different in the case of different vapors, following the orde: $CH_2Cl_2 > CHCl_3 > CCl_4$. This suggests that the response mechanism concerning the NVC effect must be related to the solvent/composites interaction. In general, in a composite with CB content lower than the percolation threshold, the CB amount is not sufficient to establish at least one conduction path throughout the matrix and the conduction is governed by tunneling effect. Accordingly, the electric resistance must be determined by the distance of the nearest CB particles. When the composites are exposed to chlorinated hydrocarbon vapors, the hydrogen bond between the matrix PEO and the filler CB formed during composite preparation (Fig. 5) is weakened and then replaced by that between PEO and the solvent molecules. Consequently, the restrain exerted by the matrix polymer on CB is released to some extent. Phase separation on a small scale can thus take place and the aggregation of the separated CB particles is facilitated, leading to decreased resistance of the composites. When the composites are removed to dry air, the solvent is desorbed and the interparticulate distance of CB must be extended again because of the rebuildup of the hydrogen bond between the matrix polymer and the conducting fillers. As a result, the electrical resistance increases to the initial value. As viewed from the principle of solvation, the ability of CH_2Cl_2 and $CHCl_3$ to form a hydrogen bond with PEO is higher than that of CCl_4. Therefore, the composites exhibit the lowest maximum NVC responsiveness in CCl_4 vapor compared to the values in CH_2Cl_2 and $CHCl_3$ vapors. Similar effects were found in alumina gel based composites.[10,11] Destruction of the hydrogen bonds between CB and the matrix due to the uptake of humidity and DMF vapor was attributed to the NVC phenomenon.

Figure 6 illustrates the time dependences of electrical response of the composites with CB content within the percolation region (i.e., 6 wt %). It is interesting to see that the responses of the composites exposed to the three vapors display different profiles with a rise in temperature. In CH_2Cl_2 and $CHCl_3$, the composites response changes from PVC to NVC as temperature increases, while the composites always exhibit PVC in CCl_4 within the same temperature range. Moreover, the critical switching temperatures corresponding to the above changes are different: the transition occurs at 35 °C for CH_2Cl_2, and at 40 °C for $CHCl_3$. The results further evidence the above-mentioned response mechanism of the composites with CB content lower than the percolation region. For the composites containing CB content within the percolation region, both tunnelling effect and interfiller contact are responsible for the electric conduction (Fig. 1). That is, the conduction is made via (i) the isolated CB particles with very narrow interfiller gap and (ii) a few conduction paths from particle-to-particle contacts.[1] An elevated temperature results in volume expansion of the composites and equivalently increases the contribution of tunnelling effect due to the enlarged interparticulate distances and the increased amount of the isolated CB particles. When the composites meet CH_2Cl_2 vapor at 30 °C, matrix swelling induced partial damage of the conduction paths plays the leading role in the response behavior of the composites and conceals the effect of CB/matrix hydrogen bonding destruction, so that PVC is measured. As temperature is raised to 35 °C, the contribution by the tunnelling effect in response to CH_2Cl_2 vapor is so prominent that the composites show NVC. For $CHCl_3$, whose ability to form hydrogen bond with PEO is lower than CH_2Cl_2, it mainly swells PEO at lower temperature and mustdestroy the hydrogen bonding between CB and PEO at higher temperature when the volume expansion of the composites is greater and the tunnelling effect is more favored. This accounts for the switching of the response habit from PVC to NVC at 40 °C in $CHCl_3$ vapor. For the same reason, since the composites with CB content of 4 wt % have rather low NVC response to CCl_4 [Fig. 4(b)], it can be expected that the response of the composites with CB content of 6 wt % against CCl_4 vapor is dominated by matrix swelling within the temperature range of interests. Therefore, no PVC/NVC transition is observed in Figure 6(c).

Based on the above discussion, the electrical response behavior of the composites against organic solvent vapors represents the change in dispersion status of CB particles in the matrix polymer or the change in structure of the conductive networks. There-
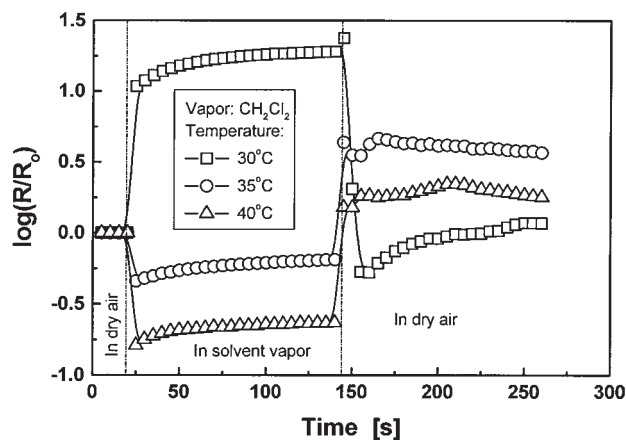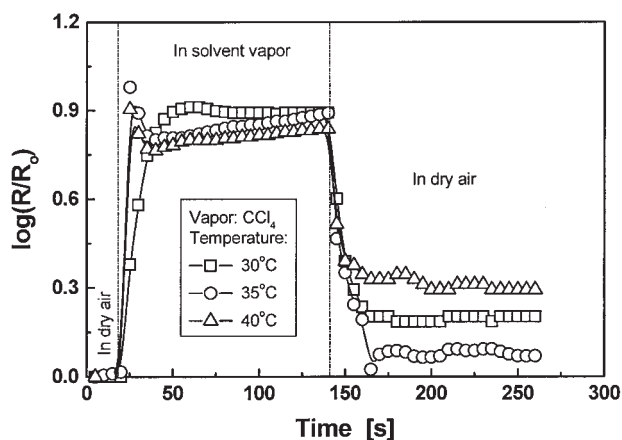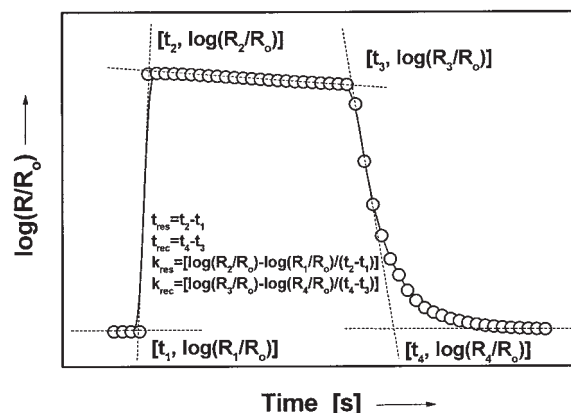
(a)
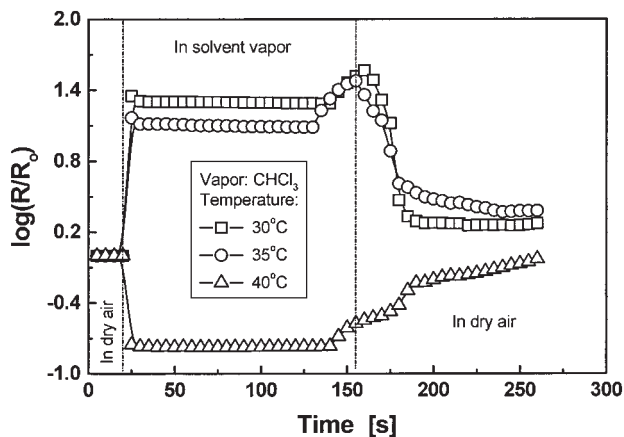
(b)

(c)

Figure 6 Resistance variation of CB/PEO composites with 6 wt % CB in response to chlorinated hydrocarbon vapors. The dashed lines define the vapor absorption and desorption zones.

Figure 7 Definitions of the composites sensitivity against organic vapor.

fore, factors such as composites microstructure, rates of vapor absorption and desorption of the composites, swelling and/or dissolving ability of a solvent, the interaction among polymer matrix, CB, and solvent, viscosity of polymer matrix, solvent properties, temperature, etc., should be considered when analyzing the composites' responsivity.

In fact, the above discussion is focused on the response mechanisms and the magnitude of responsivity, but does not deal with the time-related-sensitivity. It is worth analyzing hereinafter because it is an important aspect of sensing materials. In the current work, the composites' sensitivity is characterized by response time, t_{res}, rate of response, k_{res}, recovery time, t_{rec}, and rate of recovery, k_{rec}, respectively (Fig. 7). From the viewpoint of practical application, the composites with 10 wt % of CB are more attractive owing to their highest responsivity compared with other composites (Fig. 2). With regard to this, Table I shows the experimental results of the sensitivity parameters of the composites with CB content of 10 wt % measured at different temperatures. Both the rates of response and the rates of recovery of the composites to CH_2Cl_2 and $CHCl_3$ vapors are very fast, and the response times and recovery times are around 10 s. In addition, the latter two parameters follow the orders as a function of vapor species: t_{res} [$CHCl_3$] $< t_{res}$ [CH_2Cl_2] $< t_{res}$ [CCl_4], and t_{rec} [$CHCl_3$] $> t_{rec}$ [CH_2Cl_2] $> t_{rec}$ [CCl_4]. It should be related to the polarity of vapors and the difference of the solubility parameters between the solvents and PEO (see the $\Delta\delta$ values attached to Table I). A solvent with high polarity and solubility parameter close to matrix polymer favors to swell the composites within short time and takes a longer time to leave the composites in dry air.

On the other hand, the data in Table I indicate that the temperature dependences of response time and rate of response are different in the case of different solvent vapors. With a rise in temperature, for exam-

TABLE I
The Sensitivity Data of CB/PEO Composites with 10 wt % CB in Different Vapors[a]

Temperature (°C)	Vapors	t_{res} (s)	t_{rec} (s)	k_{res} (s^{-1})	k_{rec} (s^{-1})
30	CH_2Cl_2	8.9	11.6	0.48	0.51
	$CHCl_3$	8.7	31.6	0.55	0.15
	CCl_4	16.9	10.3	0.05	0.07
35	CH_2Cl_2	9.2	13.6	0.43	0.32
	$CHCl_3$	8.6	30.7	0.48	0.14
	CCl_4	13.8	9.5	0.09	0.13
40	CH_2Cl_2	9.5	13.5	0.42	0.31
	$CHCl_3$	8.5	39.3	0.49	0.10
	CCl_4	10.3	10.0	0.19	0.19

[a] The differences between the solubility parameters of PEO and the solvents, $|\Delta\delta|$ (absolute values), are 0.2 $J^{1/2}/cm^{3/2}$ (for $CHCl_3$), 0.62 $J^{1/2}/cm^{3/2}$ (for CH_2Cl_2), and 1.58 $J^{1/2}/cm^{3/2}$ (for CCl_4), respectively.

ple, the response time in CH_2Cl_2 increases but that in CCl_4 decreases. To have a better understanding of the phenomenon, the response times of CB/PEO composites with different CB contents (all of which are higher than the percolation threshold) in the three vapors were measured as a function of temperature. When making plots, it is found that $\ln(1/t_{res})$ varies linearly with the inverse temperature, $1/T$, regardless of whether the slopes are positive or negative. Evidently, the response processes are Arrhenius-type thermally activated ones.

These results are understandable because migration of solvent molecules in carbon black filled polymer composites belongs to Case II diffusion.[22] The matrix must relax to respond to the osmotic swelling pressure and to rearrange the macromolecular chains for accommodating the penetrant molecules. An increase in temperature would certainly accelerate the structural relaxation, and the Arrhenius relationship should be valid for the kinetics of resistance variation habit. With a rise in temperature, however, the absorbed solvent molecules also tend to leave the absorber due to the characteristics of physisorption, and hence the driving force that breaks the conducting networks is reduced accordingly. As thermal desorption kinetics can also be described by the Arrhenius equation,[23] the proportional relationships between $\ln(1/t_{res})$ and $1/T$ with positive slopes (Fig. 6) might be a reflection of this effect. On the whole, the eventual influence of temperature should result from the competition of the two opposite factors, and the controlling mechanism might be determined from the fact of whether the $\ln(1/t_{res})$ ~ $1/T$ plot has positive or negative slope.

By examining Figure 8(a), it is seen that in CH_2Cl_2 vapor only the response time of the composites with 13 wt % CB decreases with increasing temperature, while those of the composites with 9 and 10 wt % CB increase. In the case of $CHCl_3$ vapor, the response times of the composites with 10 and 13 wt % decrease with a rise in temperature [Fig. 8(b)]. When CCl_4 vapor is employed, the response times of all three com-

posites decrease with increasing temperature [Fig. 8(c)]. These results clearly suggest that the effect of solvent polarity also plays an important role. When the composites are exposed to CH_2Cl_2 vapor, the interaction between the high polarity solvent and the matrix is weakened as the temperature rises, so that the competition between adsorption and desorption delays the electrical response in the composites containing 9 and 10 wt % CB. That is, the response times of the composites must increase with increasing temperature. As for the composites with 13 wt % CB, the higher loading CB must favor solvent adsorption and the mechanism of matrix relaxation plays the leading role so that the composites exhibit accelerating effect with temperature. In the case of CCl_4 that is characterized as a nonpolar solvent, the solvent/matrix interaction is rather poor regardless of temperature. Higher temperature helps solvent diffusion into the composites and hence the response times of the composites are shortened at an elevated temperature. $CHCl_3$ possesses polarity lower than CH_2Cl_2 but higher than CCl_4. The characteristics of temperature dependences of response time of the composites in $CHCl_3$ vapor lie in the intermediary between that in CH_2Cl_2 and CCl_4.

CONCLUSIONS

1. Electrical conductive composites consisting of CB and PEO present responsivity against chlorinated hydrocarbon solvent vapors as characterized by the reversible variation in resistance. By changing CB content, vapor species, and environmental temperature, the aforesaid response behavior exhibits PVC and NVC effects alternatively. The mechanisms involved are related to the dispersion status of CB particles and solvent/composites interaction.

2. Rate of response of the composites is a function of solvent polarity, dissolution ability of solvent to matrix polymer, CB content, and environmental temperature. Effects of structural relaxation of the matrix
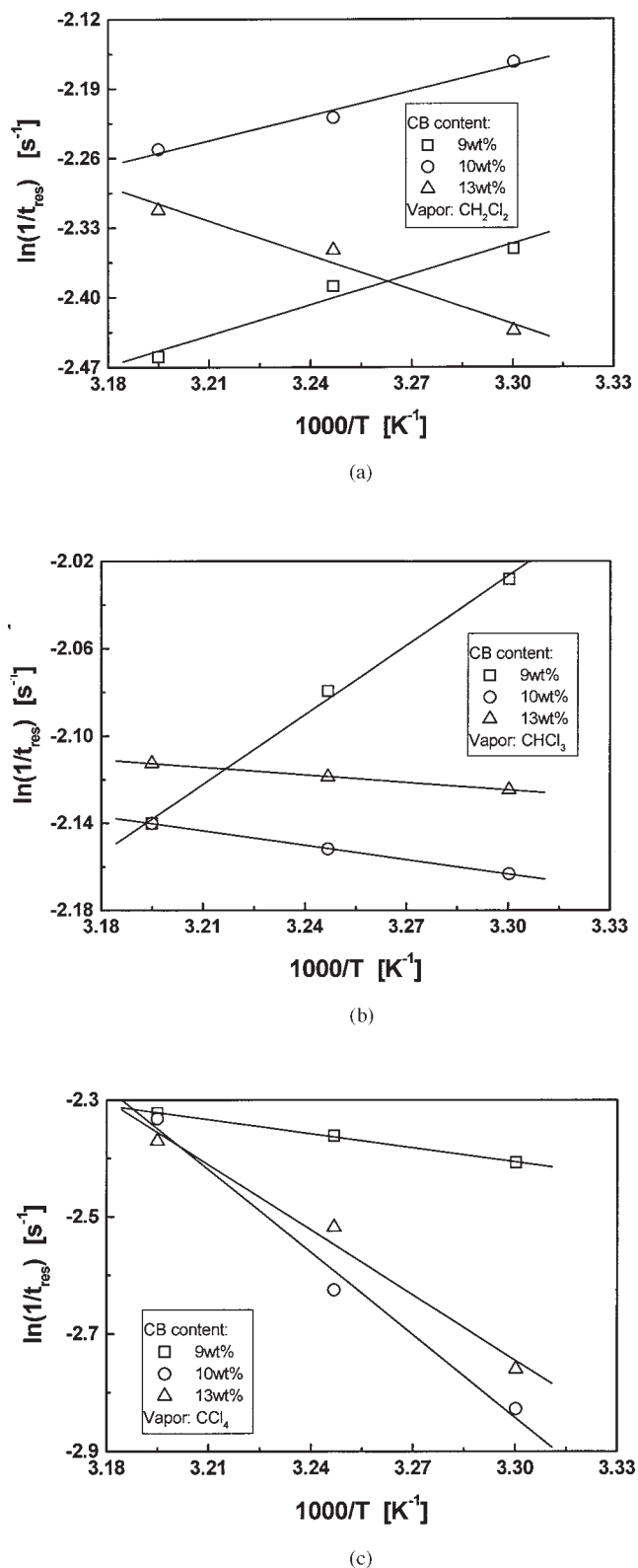
(a)

(b)

(c)

Figure 8 Arrhenius plots of response time of CB/PEO composites in chlorinated hydrocarbon vapors.

polymer and desorption of the absorbed solvent molecules lead to different dependences of response time on temperature. Depending upon the features of the possible target analytes, one might optimize the sensing materials accordingly.

References

1. Zhang, M. Q.; Zeng, H. M. In Handbook of Thermoplastics; Olabisi, O., Ed.; Dekker: New York, 1997; p 873.
2. Feller, J. F.; Lngevin, D.; Marais, S. Synth Met 2004, 144, 81.
3. Severin, E. J.; Doleman, B. J.; Lewis, N. S. Anal Chem 2000, 72, 658.
4. Burl, M. C.; Ssk, B. C.; Vaid, T. P.; Lewis, N. S. Sens Actuators B Chem 2002, 87, 130.
5. Chen, J.; Tsubokawa, N. J Macromol Sci Pure Appl Chem 2001, A38:383.
6. Chen, J.; Tsubokawa, N. Polym J 2000, 32, 729.
7. Chen, J.; Tsubokawa, N. J Appl Polym Sci 2000, 77, 2437.
8. Chen, J.; Tsubokawa, N.; Maekawa, Y.; Yoshida, M. Carbon 2002, 40, 1602.
9. Chen, J.; Maekawa, Y.; Yoshida, M.; Tsubokawa, N. Polym Adv Technol 2000, 11, 101.
10. Tsubokawa, N.; Ogasawara, T.; Inaba, J.; Fujiki, K. J Polym Sci Polym Chem 1999, 37, 3591.
11. Tsubokawa, N.; Inaba, J.; Arai, K.; Fujiki, K. Polym Bull 2000, 44, 317.
12. Breuer, O.; Tchoudakov, R.; Narkis, M.; Siegmann, A. J Appl Polym Sci 1997, 64, 1097.
13. Narkis, M.; Srivastava, S.; Tchoudakov, R.; Breuer, O. Synth Met 2000, 113, 29.
14. Dong, X. M.; Fu, R. W.; Zhang, B.; Li, J. R.; Rong, M. Z. Carbon 2003, 41, 371.
15. Dong, X. M.; Fu, R. W.; Zhang, M. Q.; Zhang, B.; Li, J. R.; Rong, M. Z. Polym Bull 2003, 50, 99.
16. Li, J. R.; Xu, J. R.; Zhang, M. Q.; Rong, M. Z. Macromol Mater Eng 2003, 288, 103.
17. Li, J. R.; Xu, J. R.; Zhang, M. Q.; Rong, M. Z. Carbon 2003, 41, 2355.
18. Dong, X. M.; Fu, R. W.; Zhang, M. Q.; Zhang, B.; Li, J. R.; Rong, M. Z. Polym Polym Compos 2003, 11, 291.
19. Dong, X. M.; Fu, R. W.; Zhang, M. Q.; Zhang, B.; Li, J. R.; Rong, M. Z. J Mater Sci Lett 2003, 22, 1057.
20. Marquez, A.; Uribe, J.; Cruz, R. J Appl Polym Sci 1997, 66, 2221.
21. Chen, S. G.; Hu, J. W.; Zhang, M. Q.; Li, M. W.; Rong, M. Z. Carbon 2004, 42, 645.
22. Dong, X. M.; Fu, R. W.; Zhang, M. Q.; Qin, Z. P.; Zhang, B.; Li, J. R.; Rong, M. Z. Polym J 2003, 35, 1003.
23. Kreuzer, H. J. Langmuir 1992, 8, 774.