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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### A NOVEL GAS SENSOR FROM POLYMER-GRAFTED CARBON BLACK: EFFECTS OF POLYMER, CRYSTALLINE ORGANIC COMPOUND, AND CARBON BLACK ON ELECTRIC RESPONSE TO TETRAHYDROFURAN VAPOR

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Online publication date: 31 March 2001

**To cite this Article** Chen, Jinhua and Tsubokawa, Norio(2001) 'A NOVEL GAS SENSOR FROM POLYMER-GRAFTED CARBON BLACK: EFFECTS OF POLYMER, CRYSTALLINE ORGANIC COMPOUND, AND CARBON BLACK ON ELECTRIC RESPONSE TO TETRAHYDROFURAN VAPOR', *Journal of Macromolecular Science, Part A*, 38: 4, 383 — 398

**To link to this Article:** DOI: 10.1081/MA-100103356

URL: <http://dx.doi.org/10.1081/MA-100103356>

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# A NOVEL GAS SENSOR FROM POLYMER-GRAFTED CARBON BLACK: EFFECTS OF POLYMER, CRYSTALLINE ORGANIC COMPOUND, AND CARBON BLACK ON ELECTRIC RESPONSE TO TETRAHYDROFURAN VAPOR

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## ABSTRACT

The responsiveness of electric resistance of three types of composites, polyethylene (PE)/PE-grafted carbon black (CB) (CB-g-PE), N,N'-dicyclohexylcarbodiimide (DCC)/CB-g-PE and PE/DCC/CB-g-PE, to THF vapor was investigated. To modify the CB compatibility in the composite, PE was grafted onto a CB surface. Although responsiveness of composite DCC/CB-g-PE was the most sensitive to THF vapor among the three composites, the composite film is too weak to be of practical use. On the contrary, the responsiveness and the sensitivity of PE/CB-g-PE were too low to be used in many fields. However, through modification by the addition of DCC, responsiveness was greatly improved, and the sensitivity was considerably higher than that of PE/CB-g-PE. The effects of CB-g-PE and DCC content in the composites on the responsiveness to THF vapor was studied in detail. It was found that the responsiveness of electric resistance to THF vapor was caused by the change of the crystalline structure of the composite. A crystalline model was proposed to explain the response of the composite to solvent vapor.

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\*Corresponding author.

*Key Words:* Carbon black; Composite; Polyethylene; Surface grafting; N,N'-dicyclohexylcarbodiimide; Gas sensor; Electric resistance.

## INTRODUCTION

In our recent studies, we found that the crystalline polymer-grafted carbon black (CB) could be used as gas sensor materials [1-6]. The gas sensor could be easily manufactured at a low cost, and the response to solvent vapor was very rapid, and sensitivity was quite high. By the use of a composite sensor, it is possible to examine and identify solvent vapors in air at room temperature under normal atmosphere [1-5] and chemical compounds in solvent [6].

As reported in the above papers, the electric resistance of the gas sensor from CB composites drastically increased when it was transferred from air to solvent vapor. It was considered that the crystallinity of matrix polymer played an important role in the response of the gas sensor. That is, the crystallinity change of the composite is considered as the main reason to cause the response.

It is well known that even after CB particles are incorporated in crystalline polymer, the polymer crystal unit cell parameters does not change, and the crystalline structure is not destroyed, which suggests that CB particles are dispersed into amorphous regions, but not crystalline regions [7-11]. In addition, according to DSC results [12], CB had no real effect on the degree of the matrix crystallinity. A CB filled amorphous region is considered to produce a continuous phase in the composite. When the composite absorbed vapor, the crystalline polymer is dissolved and cuts the CB/amorphous polymer continuous phase or CB network in the amorphous phase, leading to a large change of electric resistance of the composite.

During the manufacture of the gas sensor, the conductive polymer/CB composite film was loaded on a comb-like electrode. The composite film may be deposited, coated, or other methods, which could be applied on the substrate. The electrical response may be quantified in terms of resistance, impedance, inductance, capacitance, or other electrical changes. In this study, electric resistance of composite is selected as a response signal due to its easy measurement.

In this paper, the effect of N,N'-dicyclohexylcarbodiimide (DCC), as a crystalline organic compound, on the responsiveness of the composite from polyethylene (PE) and PE-grafted CB (CB-g-PE) is studied. It was expected that DCC incorporated into CB composite effectively increases the crystallinity of the composite, resulting in an improved response to THF vapor.

## EXPERIMENTAL

### Materials

A furnace black, Porousblack (Asahi Carbon Co. Ltd., Japan), was used as a conductive filler in the composite. The specific surface is 447 m<sup>2</sup>/g, and the aver-

age particle size is 41 nm. The content of the surface carboxyl and phenolic hydroxyl groups is 0 and 0.03 mmol/g, respectively [13, 14]. The CB was dried under vacuum at 110°C for 48 hours before use. DCC (mp = 34.5°C), used as a component of the composite, was purchased from Wako Pure Chemical Ind. Ltd., and dried under vacuum at room temperature before use. PE (Mn = 460; mp = 108°C) was purchased from Aldrich Chemical Co., and was used as received.

### Grafting of PE onto CB Surface

The surface grafting of PE onto CB was achieved by a two-step method: introduction of carboxyl groups by the treatment with 4,4'-azobis(4-cyanopen-tanoic acid) and direct condensation of carboxyl groups on CB with terminal hydroxyl groups of PE. The detailed procedures were described in the previous paper [1-6].

### Preparation of Conductive Composite Films

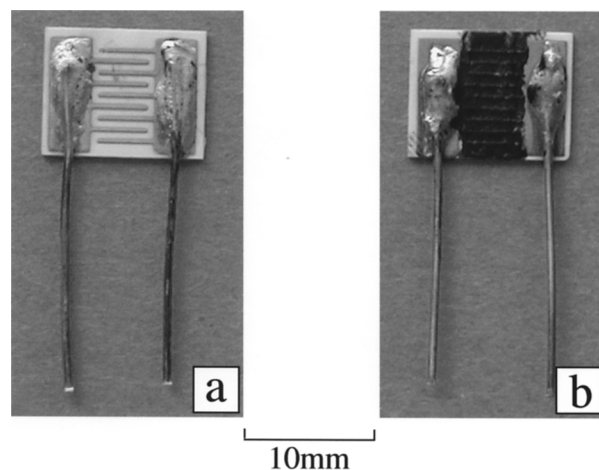
CB filled polymer composite can be formed by various techniques such as solution casting, suspension casting, and mechanical mixing. In this study, the composite film was prepared by the suspension casting method. For a typical process, 0.4 g PE or DCC (or both) and 10.0 ml of THF were added into a 100 ml flask. After complete dissolution at 65°C, CB-g-PE was added and mixed homogeneously with a magnetic stirrer. The resulting suspension was used to dip coat on a comb-like electrode.

### Preparation of Comb-like Electrode by Screen-Printing

The comb-like electrode was prepared by screen-printing of conductive Ag/Pd paste onto a ceramic plate, as shown in Figure 1(a). The size of the ceramic plate is 10 mm × 8 mm × 0.8 mm. The printed ceramic plate was then annealed in an oven at 840°C to remove the organic components from the Ag/Pd paste. It formed two comb-like electrode poles, which had four and five teeth, respectively, and bit with each other. Each of the comb-like poles was soldered with a copper wire to connect to the measurement device. Then, the composite film was coated on the teeth with the area of 4 mm × 7 mm, and the thickness was about 12 μm.

### Measurement of Electric Resistance

The electric resistance of the composite in solvent vapor was measured by hanging the electrode in a glass tube containing pure solvent at the bottom. The distance between the electrode and solvent surface is 2.0 cm. The DC electric



**Figure 1.** Comb-like electrode (a) uncoated and (b) coated with the polymer/CB-g-PE film on its plate.

resistance of the composite film was measured as a function of time. Resistance measurements were performed using a simple two-point configuration [3]. The electrode was connected directly to a digital multimeter (Advantest Co. Ltd., Japan; type R6871E-DC) via a ribbon cable, and the resistance was read by personal computer. Before the measurements, all samples were kept under vacuum at room temperature for over 24 hours. The resistance was measured in dry air and air saturated with THF vapor at 25°C.

### Responsiveness Analysis

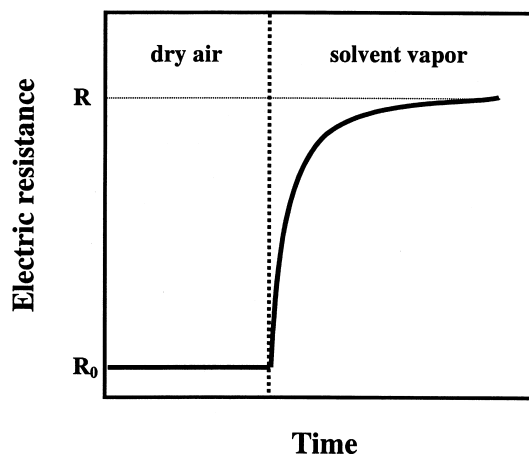
The electric resistance of the comb-like electrode was automatically recorded before, during, and after exposure to THF vapor. A typical trial consisted of 60 seconds in dry air, 300 seconds in THF vapor, and then 300 seconds in dry air again. Figure 2 shows a typical change of electric resistance of the CB-filled composite from dry air to THF vapor. In THF, the steady-state resistance value is  $R$ , while in air, its initial resistance is  $R_0$ . In this work, we define “responsiveness” as follows:

$$\text{Responsiveness} = R/R_0$$

## RESULTS AND DISCUSSION

### Sensor Material of the Composite from PE and CB-g-PE

The responsiveness of composite from low-density polyethylene (LDPE) and poly(ethylene-*block*-ethylene oxide) (PE-*b*-PEO)-grafted CB in cyclohexane

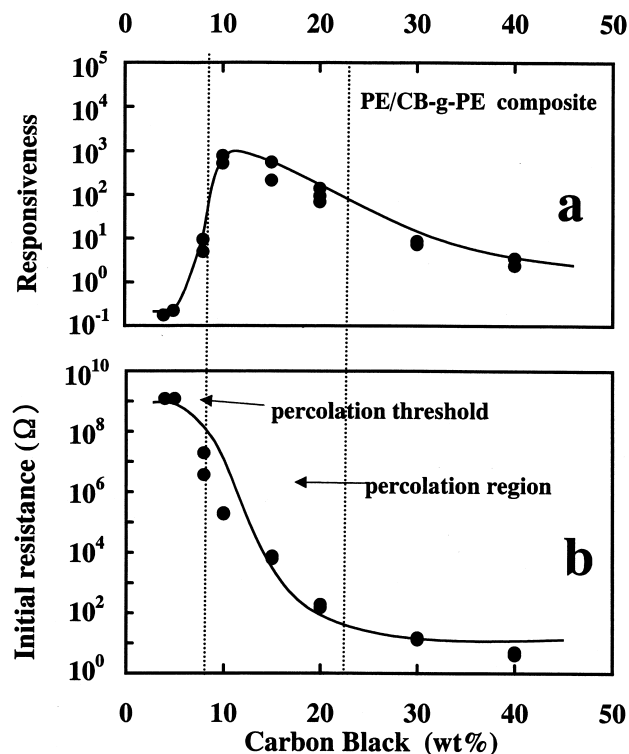


**Figure 2.** Typical changes of electric resistance of the CB-filled composite from dry air to THF vapor.

vapor [4] was higher than  $10^5$ , but in THF vapor, its responsiveness was lower than  $10^2$ . In this study, a low molecular weight ( $M_n=460$ ) PE, with terminal hydroxyl group was used. The responsiveness of the composite from PE and CB-g-PE (PE/CB-g-PE) was investigated.

Figure 3 (a) shows the effect of CB-g-PE content on the responsiveness of composite PE/CB-g-PE to the THF vapor. At lower CB-g-PE content, the responsiveness increased with the CB-g-PE content. On the contrary, at higher CB-g-PE content, the responsiveness decreased with the increase in CB-g-PE content. The maximum responsiveness, about  $10^3$ , was observed around 12% of CB-g-PE content. It is interesting to note that at very low CB-g-PE content, responsiveness was less than 1, which means the electric resistance of the composite in THF vapor decreases compared with its initial value, showing a “negative response”. In the case of high CB-g-PE content (over 30 wt%), the responsiveness of the composite in THF vapor was less than 10.

Figure 3 (b) shows the initial resistance ( $R_0$ ) of the above composite. It was clear that the initial resistance decreased with an increase in CB-g-PE content. At very low CB-g-PE content, the initial resistance is very high, over  $1200 \text{ M}\Omega$  (the maximum resistance we can measure with our multimeter). When the CB-g-PE content was higher than a certain level, the  $R_0$  began to decrease. This CB-g-PE content is generally called percolation threshold. In comparison with the responsiveness curve, when the CB-g-PE content was lower than the percolation threshold, responsiveness was lower than 1, and the composite exhibited a “negative response”. The phenomenon is similar to the results of the composite from poly(ethylene oxide) (PEO) and PEO-grafted CB [5]. The decrease of electric resistance in THF is caused by the CB rearrangement. The change of electric properties is explained by tunneling conduction in the composite [5, 15].



**Figure 3.** Effect of CB-g-PE content on (a) responsiveness to THF vapor and (b) initial resistance of the composite PE/CB-g-PE.

Over the percolation threshold, the initial resistance decreased sharply with increasing CB-g-PE content, whereas at higher CB-g-PE content, the resistance almost remained constant with the change of CB-g-PE content. The  $R_0$  decreasing region is usually called percolation region. In this region, the dispersion of CB changes from an individually isolated state to a network state, leading the composite to turning from insulator to conductor. However, in this percolation region, the conductive network was unstable, and could be easily destroyed even by the slight change of any component or condition, such as CB dispersion and content, temperature, pressure, and vapor absorption. As shown in Figure 3, the CB-g-PE content at the percolation threshold of the composite PE/CB-g-PE is about 6 wt%, and in the percolation region, 6-20 wt%.

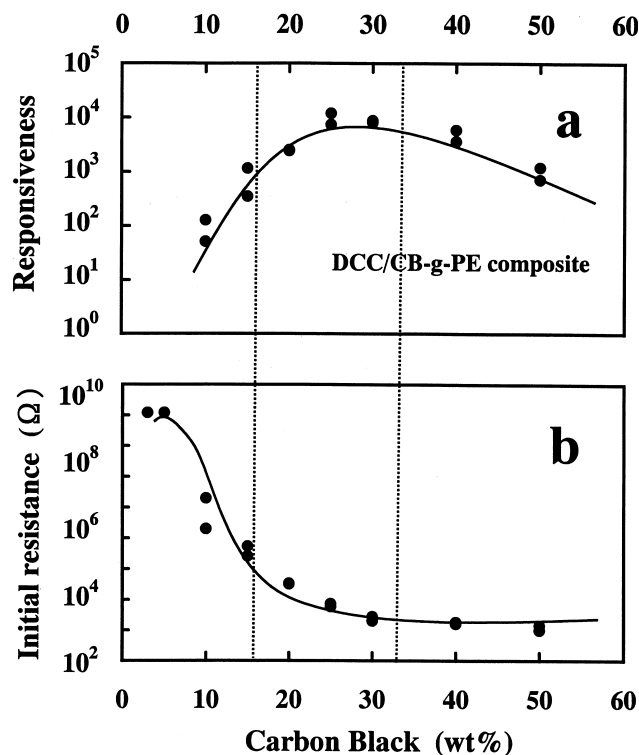
### Sensor Material of the Composite from DCC and CB-g-PE

The conducting composite of CB/polymer, as a PTC (positive temperature coefficient) material [16-19] or as a gas sensor [20-23] has been studied intensively. However, the composite from organic compound and CB has been studied little as yet. One possible reason may be due to its poor mechanical strength.

In this work, to study the effect of crystallinity on the responsiveness of the composite to THF vapor, DCC was selected as a matrix with good crystallinity. The composite film from DCC and CB-g-PE (DCC/CB-g-PE) was successfully prepared. As shown in Figure 4, responsiveness to THF vapor of the composite DCC/CB-g-PE was similar to that of the composite PE/CB-g-PE (as shown in Figure 3).

However, the maximum responsiveness of the composite was considerably larger than that of PE/CB-g-PE, and the change of the responsiveness with the CB-g-PE content was not as steep. It is considered that in the composite PE/CB-g-PE, CB particles are loaded in the amorphous region, but in the composite DCC/CB-g-PE, CB is only loaded in the interface of DCC crystalline grains.

When the composite is exposed to THF vapor, some of the DCC crystalline grains absorb the vapor and are dissolved, and become liquid with low viscosity. The aggregation of CB particles in the interface of DCC crystalline was easily cut by the liquid. On the contrary, CB particles in amorphous region of PE are bound together by a polymer chain. Although the crystalline polymer absorbed solvent, the CB network was not easily cut because of the high viscosity of the polymer matrix. Therefore, even in THF vapor, the CB network in the composite PE/CB-g-PE was still maintained, resulting in the low responsiveness.



**Figure 4.** Effect of CB-g-PE content on (a) responsiveness to THF vapor and (b) initial resistance of the composite DCC/CB-g-PE.



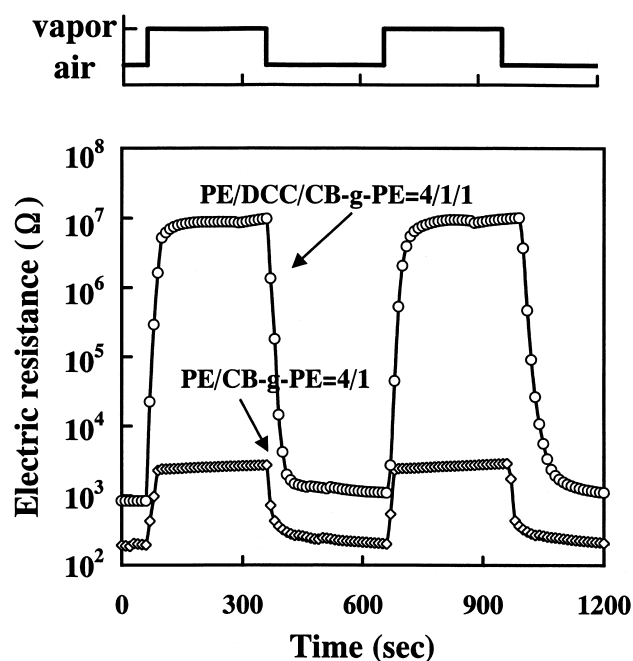
### Sensor Material of Composite from PE, DCC and CB-g-PE

The composites from polymer and polymer-grafted CB can be used as gas sensor material because it forms a strong enough film and responds to solvent vapors with high sensitivity [1-5]. As mentioned above, though the composite PE/CB-g-PE can form strong film to be loaded on the comb-like electrode, responsiveness to THF vapor was lower than 1000. Especially, at high CB content over 20 wt%, responsiveness was too low to be used as THF vapor sensor material. On the other hand, as shown in Figure 4, the responsiveness of the composite DCC/CB-g-PE was higher than 1000 in a wide CB content range, but the composite was not strong enough.

Therefore, it is expected that the responsiveness of composite PE/CB-g-PE is improved by the addition of DCC. Figure 5 shows the response of the composite PE/DCC/CB-g-PE and PE/CB-g-PE to THF vapor. The weight ratio of PE vs. DCC vs. CB-g-PE in the PE/DCC/CB-g-PE is 4 vs. 1 vs. 1, and PE vs. CB-g-PE in the PE/CB-g-PE was 4 vs. 1.

The composite was exposed to dry air for 60 seconds to obtain the initial resistance. One cycle of the resistance record processing consisted of a 300 second exposure to THF vapor, and then a 300 second exposure to dry air.

It was found that the resistance of the composite PE/CB-g-PE and PE/DCC/CB-g-PE drastically increased when the composites were transferred



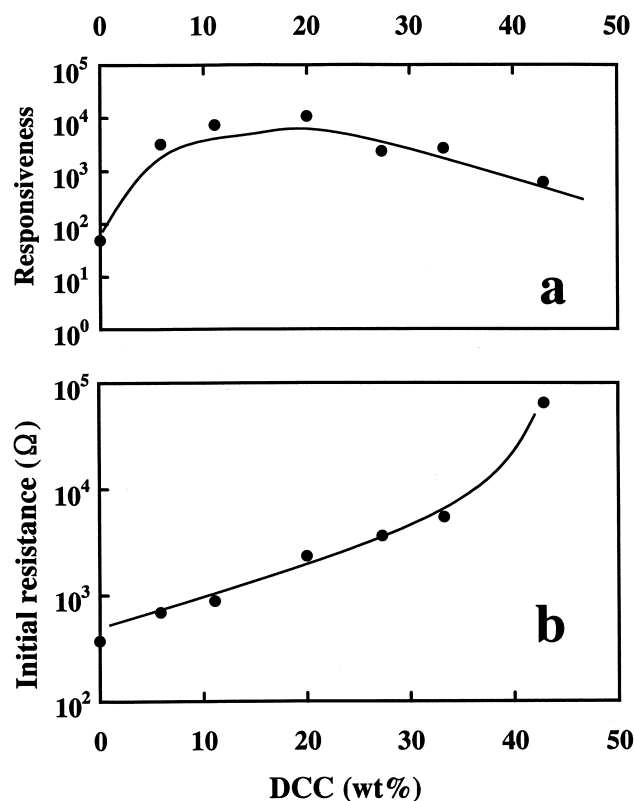
**Figure 5.** Electric resistance of the composite PE/CB-g-PE and PE/DCC/CB-g-PE recorded in dry air and THF vapor.

from dry air to THF vapor, and decreased quickly to their initial value when they were returned to dry air. It was interesting that responsiveness of the composite PE/DCC/CB-g-PE is much larger than that of PE/CB-g-PE.

It seems that DCC plays an important role in responsiveness of composite PE/DCC/CB-g-PE to THF vapor. The responses of electric resistance of PE/CB-g-PE and PE/DCC/CB-g-PE were reproducible even after exposure to THF vapor and dry air over 30 circles. It was still very stable even after exposure to THF vapor for several days.

When DCC was added into the composite PE/CB-g-PE, one might note that the CB content decreased in the composite, which could increase the responsiveness of PE/CB-g-PE. Actually, by the addition of DCC, the CB content is decreased from 20 wt% to 14.4 wt%. However, as shown in Figure 3, when CB content was 14.4-20 wt%, the responsiveness change is not more than one order of magnitude.

To estimate the effect of DCC on the responsiveness, the relationship between the amount of DCC and the responsiveness of the composite to THF vapor was studied in detail. As shown in Figure 6(a), at low DCC content to



**Figure 6.** Effect of DCC content on (a) responsiveness to THF vapor and (b) initial resistance of the composite PE/DCC/CB-g-PE under fixed PE/CB-g-PE ratio 4 vs. 1.

PE/CB-g-PE (20 wt% CB), the responsiveness increased with increasing the DCC content. When DCC was about 20%, responsiveness reached a maximum. Then, responsiveness decreased slowly with the increase of CB-g-PE content. The maximum responsiveness was about 10000, which was fairly higher than that of PE/CB-g-PE.

Figure 6 (b) shows the relationship between initial resistance of the composite PE/DCC/CB-g-PE and DCC content. The logarithm of initial resistance increased linearly with increasing CB-g-PE content up to 35 wt% of DCC content, and then increased drastically, indicating the existence of a similar percolation threshold. It seems that the maximum responsiveness observed in Figure 6 (a) does not affect the relationship between the DCC content and initial resistance. However, at a high DCC content, the initial resistance was very high and DCC influenced the composite response, leading a slow decrease of responsiveness at high DCC content.

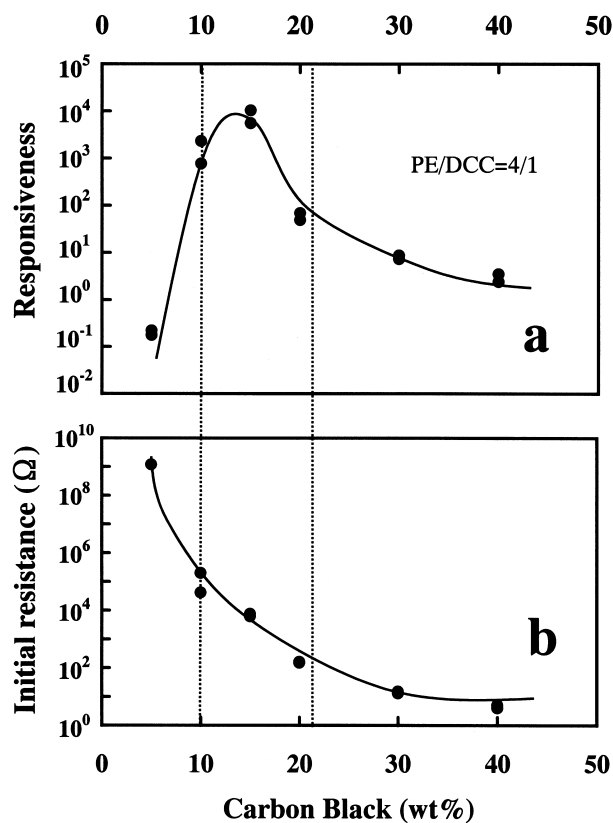
Moreover, in a fixed ratio of PE and DCC in 4 vs. 1, the effect of CB-g-PE on the responsiveness and initial resistance was also investigated. As shown in Figure 7, responsiveness and initial resistance change with CB content was very similar to the results from PE/CB-g-PE as shown in Figure 3. But in the same CB content, the responsiveness of PE/DCC/CB-g-PE was larger than that of PE/CB-g-PE. This indicates that the PE/DCC/CB-g-PE responds to THF vapor with a much larger responsiveness at the optimum CB content.

For the composites PE/DCC/CB-g-PE, at very low CB content, it was also observed that the resistance decreased when the composite was transferred from dry air to THF vapor. At high CB content, the increase of resistance in THF vapor was less than one order of magnitude.

In addition, as shown in Figure 7, the maximum responsiveness is also located in the end of the percolation region. At the same CB content, the initial resistance of PE/CB-g-PE and PE/DCC/CB-g-PE was almost equal to each other, meaning that the partial PE in composite replaced by DCC did not influence the initial resistance distinctly.

### Crystalline Model Explanation

Theoretically, the increase of electric resistance is considered to be responsible for the swelling of the matrix in the composite by absorption of solvent [21-25]. However, in general, the decrease of the CB volume fraction caused by the swelling of polymer is less than several percent. So, the large increase of electric resistance due to the slight change of CB volume fraction was considered to occur only at the percolation region. Doleman *et al.* also reported that the increase of electric resistance of the composite is caused by the swelling of the polymer when the polymer absorbed vapors [21, 22]. They proposed that the large response is located at the percolation region, but the effects of CB content on responsiveness have not been reported in detail.

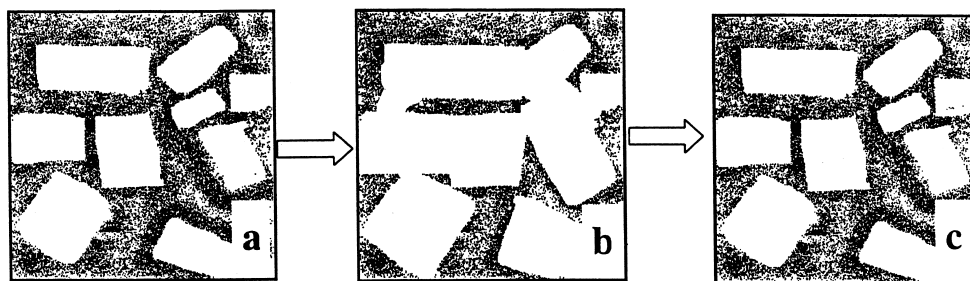


**Figure 7.** Effect of DCC content on (a) responsiveness to THF vapor and (b) initial resistance of the composite PE/DCC/CB-g-PE under fixed PE/DCC ratio 4 vs. 1.

However, the polymer swelling theory could not explain the very small increase of electric resistance exhibited by the CB filled polymers when they were strained to an extent equivalent of that found in the solvent vapor [20, 26]. It also could not explain the fairly large responsiveness even though the CB content was much higher than the percolation threshold, as shown in Figures 3, 4, and 7.

Accordingly, we doubted the swelling theory. It was also doubted by Meyer [25], since he found that some composites had a quite large resistance change at their melting point, but their volume swellings were small. In our gas sensor studies [3-5], the change of the polymer crystalline structure, including the swelling in volume and the flow of the dissolved crystalline polymer, was considered to make a drastic change in electric resistance. Especially, the flow of the dissolved crystalline compound may be the main reason for the large change of the composite resistance.

In this work, the crystalline model was applied to explain the results of this experiment as shown in Figure 8. In the model, three phases are considered in the polymer/CB composite, i.e., crystalline phase, CB phase, and amorphous phase.



**Figure 8.** A crystalline model for explanation of conduction-insulation changes of a CB composite. Composite in (a) dry air, (b) solvent vapor, and (c) dry air again.

In dry air at room temperature, CB was only distributed in a continuous amorphous phase. Therefore, the composite was composed of a conductive part (CB-dispersed amorphous polymer) and insulation part (crystalline phase).

As shown in Figure 8(a), when the conductive part was continuous, and the CB content in this part was over percolation threshold, the composite was in a conducting state. However, if the CB content was lower than the percolation threshold, or the conductive part was not continuous, the composite was the insulator, and thus, electric resistance was very high.

To simplify the model, the CB content in amorphous phase was assumed to be higher than the percolation threshold. Therefore, the amorphous phase was conductive. In this case, the crystalline area-like islands dispersed in the composite, as shown in Figure 8 (a), to give an island-ocean construction structure.

When the composite absorbed solvent vapor, the crystalline structure in the composite was destroyed, resulting in the crystalline polymer chain being swollen and moveable. As shown in Figure 8(b), the dissolved crystalline compound will be covered onto the CB surface, and thus some of the contact CB particles would be separated. Therefore, the electric resistance of the amorphous region (the initial conductive region) may increase drastically. On the other hand, the continuous conductive phase is cut and changes into island-like construction, since the dissolved crystalline phase was changed into ocean form. In the above two cases, the composite was in an insulation state and, thus the electric resistance increased drastically by several orders of magnitude.

When the composite was transferred from THF vapor to dry air, the absorbed THF by crystalline grains was desorbed as shown in Figure 8(c), and the polymer was recrystallized and shrunk, resulting in the isolation of the insulation part and the re-continuity of the conductive part. Therefore, the electrical resistance could return to its initial value.

In the case of DCC/CB-g-PE, there were some differences from the above model, because there was no amorphous phase in the composite. CB particles are considered to be loaded in the interface of DCC crystalline grains and formed a line construction throughout the whole composite. Therefore, the continuous conductive part was the compressed CB aggregations by DCC crystalline grains.

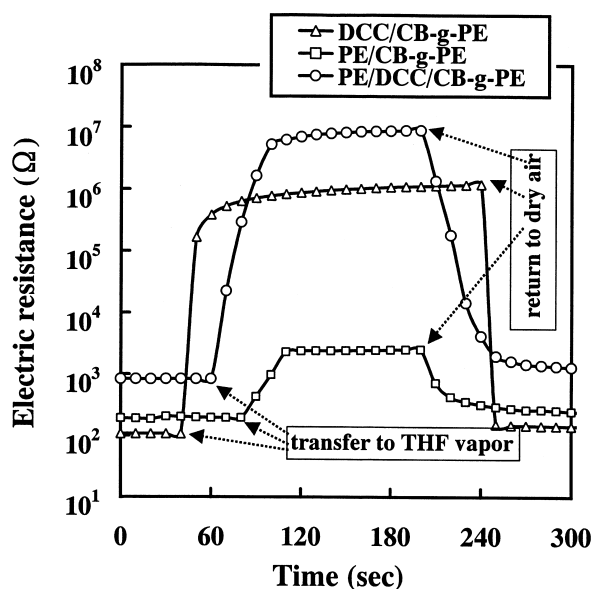
In the composite DCC/CB-g-PE, when the CB aggregations compressed by DCC crystalline grains are connected with each other only by physical force, it is expected that the CB conductive network was narrow and weak. Therefore, the response of electric resistance was very sensitive to solvent vapor, as the absorbed vapor easily destroys the weak CB network, resulting in a large change of electric resistance of the composite.

### Sensitivity of Response of the Composites

As shown in Figure 9, when the composite DCC/CB-g-PE was transferred from dry air to THF vapor, the electric resistance increased in four orders of magnitude within 10 seconds, while in the composite PE/DCC/CB-g-PE, which shows the same change of electric resistance, it took 40 seconds. For PE/CB-g-PE, the response was so insensitive that it took 30 seconds.

Although the DCC/CB-g-PE responsiveness was the most sensitive to THF vapor among the three composites, the composite film is too weak for practical use. On the contrary, the responsiveness and the sensitivity of PE/CB-g-PE were too low to be used in many fields. However, through modification by the addition of DCC, responsiveness was largely improved, and the sensitivity was also higher than that of PE/CB-g-PE.

In addition, when the composites returned to dry air, as shown in Figure 9, a similar resistance change occurred. That is, the resistance of DCC/CB-g-PE re-



**Figure 9.** The changes of electric resistance when the composites were transferred from dry air to THF vapor, and then in dry air again.

turned to its initial value very quickly with only 10 seconds. But, for PE/DCC/CB-g-PE and PE/CB-g-PE, it took 40 seconds, and 30 seconds, respectively.

The decrease of electric resistance, when the composites were transferred from THF vapor to dry air could also be explained by the crystalline model.

There are two parts in the composite PE/CB-g-PE: crystalline PE and CB-g-PE filled amorphous PE. In THF vapor, as shown in Figure 8(b), the crystalline PE absorbed vapor and swelled, resulting in a continuous phase in the composite. In this case, CB-g-PE filled amorphous phase was cut and turned into isolated, leading to its large electric resistance. But when the composite was transferred to dry air, as shown in Figure 8(c), the THF vapor desorbed from the PE crystal was slow. Thus, the transition from the swelling of the crystalline PE to a shrunken state, took a long time in accordance with a slow reverse of electric resistance as shown in Figure 9.

In the case of the composite DCC/CB-g-PE, the absorbed THF vapor was easily desorbed and the DCC recrystallized quickly, because of the low molecule weight of DCC. It resulted in the CB particles loaded again in the interface of DCC crystal grains. Thus, the electric resistance returned to initial value very quickly.

For the composite PE/DCC/CB-g-PE, the crystalline part included crystalline PE and DCC. As the DCC recrystallized quickly, there was a drastic decrease of the electric resistance at the initial 10 seconds when the composite was returned to dry air. But in the following 30 seconds, the recovery of electric resistance become slow since the desorption of the THF vapor from PE and recrystallization of PE are slow. Moreover, the addition of the DCC crystalline compound to PE/CB-g-PE greatly improved its responsiveness to the THF vapor. This may imply that the crystalline region of the conducting composite played an important role in the responsiveness to the THF vapor.

## CONCLUSION

The composite DCC/CB-g-PE had the largest responsiveness, but its low strength limited its practical use. On the other hand, the responsiveness of PE/CB-g-PE was too low to be used as a THF sensor. By the addition of DCC into PE/CB-g-PE, its responsiveness to THF vapor was greatly improved.

To a composite of PE/CB-g-PE, with the ratio of PE and CB-g-PE being 4 vs. 1, the responsiveness to THF vapor was less than  $10^2$ . However, with the addition of DCC, the responsiveness could be improved, especially, when the DCC content in the composite with 20 wt%, the responsiveness to THF vapor was drastically improved to  $10^4$ .

We proposed a crystalline model to explain the change of electric resistance when the composite was transferred between dry air and THF vapor. In dry air, the crystalline region was isolated in the amorphous region, forming an island-ocean construction. In THF vapor, the crystalline absorbed the vapor, resulting in the

swelling of the volume and the flow of the polymer chain. So the amorphous PE/CB-g-PE was cut and became isolated, and a large increase of electric resistance occurred. When the composite was returned to dry air, the dissolved crystalline part can re-crystallize and shrink to the original state, resulting in the resistance returning to its initial value.

The higher the crystallinity, the higher the composite responded to vapor. The addition of DCC into PE/CB-g-PE may be regarded as the increase of crystallinity of the composite. Therefore, it is expected that the addition of a organic crystalline compound to polymer/CB-g-PE composite improves responsiveness to vapor when the composite is used as gas sensor material.

### ACKNOWLEDGMENT

This study was partly supported by a Grant-in-Aid for Scientific Research (No. 11650708) from the Ministry of Education, Science, Sports and Culture of Japan.

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Received June 15, 2000