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A novel gas sensor from crystalline polymer-grafted carbon black: responsibility of electric resistance of composite from crystalline polymer-grafted carbon black against solvent vapor

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Summary

Crystalline polymers, such as poly(ε-caprolactone) (PCL), poly(ethylene adipate) (PEA), and polyethylene (PE), were successfully grafted onto carbon black surface by direct condensation of terminal groups of these polymers with carboxyl groups on the surface using N,N'-dicyclohexylcarbodiimide as a condensing agent. The electric resistance of a composite prepared from these crystalline polymer-grafted carbon black drastically increased to 104-105 times of initial resistance in good solvent vapor of grafted polymer and returned to initial resistance when it was transferred into dry air. However, the change of electric resistance of the composite hardly observed in poor solvent vapor. These results suggest that these composite can be applied as a novel gas sensor.

Introduction

In a series of our papers, we have succeeded in the grafting of various vinyl polymers onto carbon black surface by the polymerization of vinyl monomers initiated by initiating groups, such as azo (1) or peroxyester (2), potassium carboxylate (3) and acylium perchlorate groups (4) introduced onto the surface. The grafting of polymers onto carbon black surface was also achieved by the direct condensation of carboxyl groups on the surface with polymers having terminal hydroxyl and amino groups in the presence of condensing agents (5,6). These polymer-grafted carbon blacks thus obtained were easily and uniformly dispersed in polymer matrices (7-9).

It is well known that a composite from vinyl polymer-grafted carbon black and vinyl polymer shows a large positive temperature coefficient of electric resistance, i.e., PTC, at near the glass transition temperature of the matrix polymer (10-13). Recently, we pointed out that the electric resistance of the composites prepared from crystalline polymers and these polymer-grafted carbon blacks drastically increases about 10^4-10^5 times of initial resistance at the melting point of crystalline polymer (14,15). These phenomena may be due to a widening of the gaps between the carbon black particles by melting of crystalline polymer matrix.

More recently, we have pointed out that the electric resistance of a composite prepared from crystalline polyethyleneimine (PEI)-grafted (16) and poly(ethylene glycol) (PEG)-grafted carbon black (17) drastically increased to 10^4-10^5 times of initial resistance in methanol, ethanol, and water vapor, which are good solvent of PEI and PEG. But the change of electric resistance of the composite hardly observed in n-hexane and toluene vapor, which are non-solvent of PEI and PEG. These results suggests the possibility of detection of a slight change of crystalline structure of these polymers by the absorption of solvent as a large increase of electric resistance of the composite.

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Table 1 Properties of carbon black used

Porousblack	Specific surface area (m^2/g)	Particle size (nm)	OH group (mmol/g)	COOH group (mmol/g)
Untreated	447	41	0.03	0
ACPA-treated	447	41	0.03	0.08

In the preceding paper, the grafting of poly(ε-caprolactone) (PCL), poly(ethylene adipate) (PEA), and polyethylene (PE) onto carbon black surface and the responsiveness of electric resistance of the composites prepared from these crystalline polymer-grafted carbon black against solvent vapor and humidity were investigated.

Experimental

Materials

Conductive carbon black used was furnace black, Porousblack, obtained from Asahi Carbon Co. Ltd., Japan. The properties of the carbon black were shown in Table 1. The content of carboxyl (COOH) and phenolic hydroxyl (OH) groups was determined by use of sodium bicarbonate (18) and 2,2-diphenyl-1-picrylhydrazyl (19), respectively. The carbon black was dried in vacuo at 110°C for 48 h before use.

4,4'-Azobis(4-cyanopentanoic acid) (ACPA) obtained from Wako Pure Chemical Ind. Ltd., Japan was recrystallized from methanol. N,N'-Dicyclohexylcarbodiimide (DCC) obtained from Wako Pure Chemical Ind. Ltd., was dried in vacuo at room temperature. Tetrahydrofuran (THF), ethyl acetate, toluene, and other solvents were purified by ordinary methods. Butane and propane gas used were commercially available fuel gas and used without further purification.

Crystalline polymers

PCL ($Mn=1.2x10^3$), PEA ($1.0x10^4$) and oxidized PE ($Mn=1.3x10^3$) were obtained from Aldrich Chemical Co. These polymers were used without further purification and dried in vacuo at 80°C before use.

Introduction carboxyl groups onto carbon black surface

The introduction of carboxyl groups onto carbon black surface was achieved by the trapping of radicals formed by the thermal decomposition of ACPA. The detailed procedures were described in the previous paper (20).

Grafting of crystalline polymer onto carbon black surface

The grafting of PCL, PEA, and PE onto carbon black surface was achieved by the direct condensation of carboxyl groups on the surface with terminal hydroxyl groups of these polymers using DCC as a condensing agent (5, 16, 17). A typical example is as follows. Into a flask, 0.25 g of carbon black treated with ACPA, 1.0 g of polymer, 25 mg of DCC, and 20.0 ml of THF were charged and the reaction mixture was stirred with a magnetic stirrer under nitrogen at 60°C for 48 h. After the reaction, the mixture was centrifuged at $1.5x10^4$ rpm and the supernatant solution was removed by decantation. The resulting carbon black was dispersed in good solvent for the polymer and the dispersion was centrifuged again. The procedures were repeated until no more polymer could be detected in the supernatant solution. The percentage of grafting was determined by the following equation:

$$\text{Grafting (\%)} = (A/B) \times 100$$

where A is weight of polymer grafted and B is weight of carbon black charged: the amount of grafted polymer, A, was estimated from weight loss when polymer-grafted carbon black was heated at 500°C by a thermal analyzer.

Preparation of composite resistor from polymer-grafted carbon black

The preparation of composite resistor paste from crystalline polymer and the polymer-grafted carbon black was carried out as follows (5,16,17).

Into a test tube, 0.25 g of polymer-grafted carbon black was dispersed in a small amount of THF and 1.00 g of crystalline polymer was added. The mixture was stirred with a magnetic stirrer at room temperature to produce a paste of the composite.

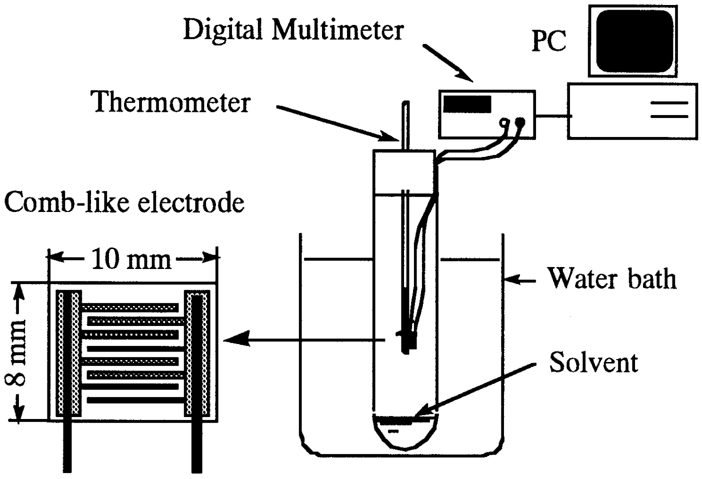


Fig.1 Comb-like electrode and apparatus for the measurement of electric resistance

Measurement of electric resistance

The measurement of electric resistance of composite resistor was carried out as follows. The composite paste was coated onto a comb-like electrode, which was prepared by the screen printing of conductive Ag/Pd paste onto a ceramic plate, and dried at 40°C. The comb-like electrode used in this study was shown in Figure 1. The electric resistance under various vapor was measured by hanging the composite resistor in a glass container containing organic solvent or water at the bottom as shown in Figure 1.

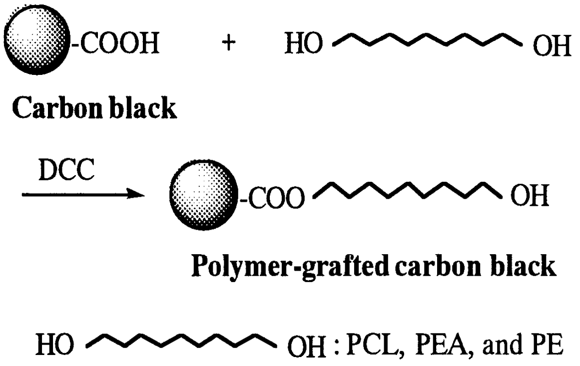
The electric resistance was measured at 25°C by use of a digital multimeter (Advantest Co. Ltd., Japan: type R6871E-DC).

Results and discussion

Grafting of crystalline polymer onto carbon black surface

The grafting of PCL, PEA, and PE onto carbon black surface by direct condensation of surface carboxyl groups with terminal hydroxyl groups of these polymers in the presence of DCC was examined (Scheme 1). In general, conductive carbon blacks such as Porousblack have no carboxyl groups. Therefore, the introduction of carboxyl groups onto carbon black was achieved through the trapping of 4-cyanopentanoic acid radicals formed by the decomposition of ACPA by carbon black surface (20). The carboxyl group content of ACPA-treated carbon black was determined to be 0.08 mmol/g by titration as shown in Table 1.

Table 2 shows the results of grafting of PCL, PEA, and PE onto carbon black surface. In the absence of DCC, the grafting of these crystalline polymers onto carbon black surface scarcely observed. On the contrary, the grafting of these polymers successfully proceeded in the presence of DCC as a condensing agent. These results indicate that polymers are grafted with ester bonds.



Scheme 1 Grafting of crystalline polymers onto carbon black by direct condensation

No gelation during the above grafting reaction was observed. This may be due to the fact that a large excess of crystalline polymers is reacted with surface carboxyl groups on carbon black. The same tendency

Table 2 Grafting reaction of crystalline polymers with carboxyl groups of carbon black by direct condensation using DCC

Grafted polymer	$\frac{Mn}{10^3}$	Grafting (%)	
		Non-catalyst	DCC
PCL	1.2	trace	9.4
PEA	10.0	trace	16.8
PE	1.3	trace	15.9

Carbon black, 0.25 g; polymer, 1.0 g; DCC, 25 mg; THF, 20 mL; 60°C; 48 h.

was reported in the reaction of functional polymers with surface functional groups on carbon black (5,6,21).

These crystalline polymer-grafted carbon blacks readily and uniformly dispersed in good solvents for grafted polymer and polymer matrices.

Electric resistance of PCL-grafted carbon black in various vapor

Figure 2 shows the effect of various vapor on the electric resistance of composite from PCL-grafted carbon black at 25°C. It is interesting to note that the electric resistance of the composite drastically increased in THF, ethyl acetate, and methanol vapor, which are good solvent for PCL and returned to almost initial resistance when it was transferred into dry air. On the contrary, the electric resistance hardly changed in humidity and n-hexane vapor, which are non-solvent of PCL. The same tendency was observed in the composite from PEI-grafted (16) and PEG-grafted carbon black (17).

This is due to a slight change of gaps between carbon black particles based on the absorption of vapor of good solvent by PCL. These results suggests the possibility of detection of a slight change of crystalline structure of PCL by the absorption of solvent as a large change of electric resistance of the composite.

Electric resistance of PEA-grafted carbon black in various vapor

Figure 3 shows the effect of various vapor on the electric resistance of composite from PEA-grafted carbon black at 25°C. The resistor has an ability to respond to not only THF but also ester, such as methyl acetate. On the contrary, the electric resistance hardly changed in humidity and n-hexane vapor.

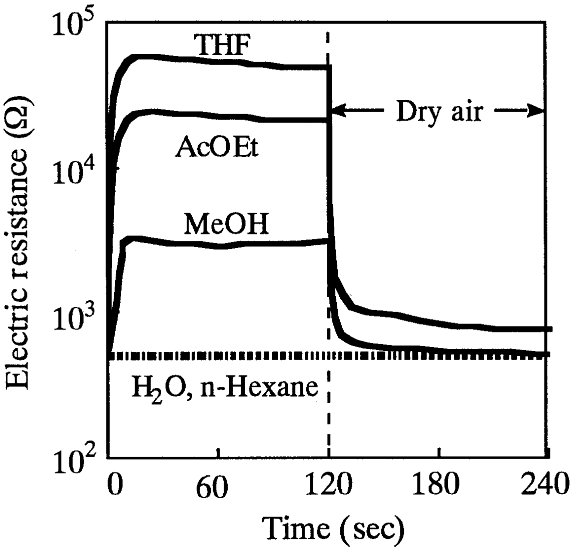


Fig. 2 Effect of various vapor on the electric resistance of composite prepared from PCL-grafted carbon black

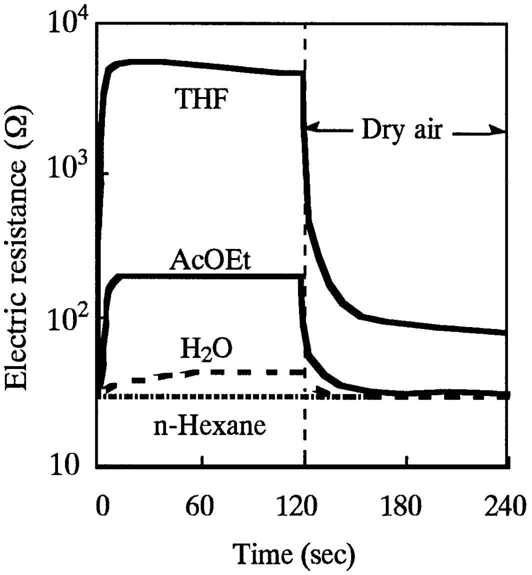


Fig. 3 Effect of various vapor on the electric resistance of composite prepared from PEA-grafted carbon black

Electric resistance of PE-grafted carbon black in various vapor

Figure 4 shows the effect of various vapor on the electric resistance of composite from PE-grafted carbon black at 25°C. The electric resistance of the composite drastically increased in THF, toluene, petroleum ether, and n-hexane vapor, which have affinity with PE, and immediately returned to initial resistance when the composite was transferred in dry air. On the contrary, the electric resistance hardly changed in polar solvent vapor, such as water and methanol vapor

In addition, the resistor of PE-grafted carbon black has an ability to respond to kerosene vapor and butane gas as shown in Figure 5. The responsibility to propane gas was very small and the electric resistance hardly changed in natural liquid gas (LNG).

Relationship between electric resistance of composite from PE-grafted carbon black and partial pressure of THF vapor

The relationship between electric resistance of the composite from PE-grafted carbon black and partial pressure of THF in mixture of water vapor in air was examined under atmospheric pressure at 25°C. The result was shown in Figure 6. It was found that the logarithm of electric resistance of the composite from PE-grafted carbon black is linearly proportional to partial pressure of THF in the mixture vapor. This indicates that the composite can be applied as a novel sensor of THF vapor.

Mechanism of gas sensing

The responsibility of these crystalline polymer-grafted carbon black to good solvent vapor lost at above melting point of the polymer as mentioned in the previous paper (17). The electric resistance of the composite from amorphous polyester-grafted carbon black hardly responded to good solvent vapor.

In addition, it was found that by exposure of the composite to good solvent vapor, few percent of weight increase was observed. And it was confirmed the adsorbed vapor was completely desorbed under dry air.

Based on the above results, crystalline structure of grafted polymer on the surface plays an important role in the increase of electric resistance in solvent vapor.

These phenomena may be due to a slight change of gaps between carbon black particles based on the absorption of vapor of good solvent by crystalline polymers. These results suggests the possibility of detection of a slight change of crystalline structure of crystalline polymer by the absorption of solvent as a large change of electric resistance of the composite.

Furthermore, it is concluded that the composite form crystalline polymer-grafted carbon black can be applied as a novel gas sensor.

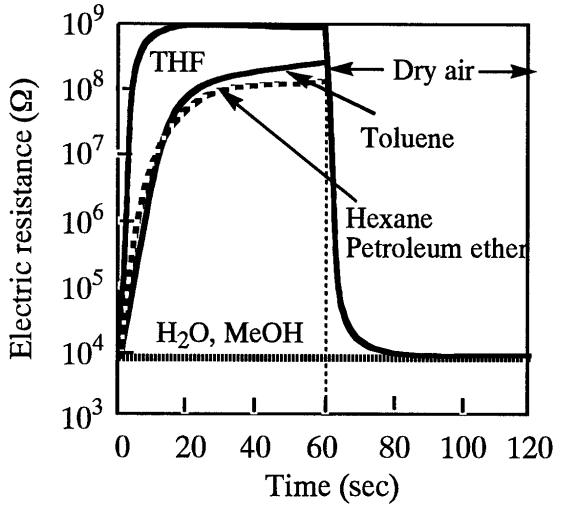


Fig. 4 Effect of various vapor on the electric resistance of composite prepared from PE-grafted carbon black

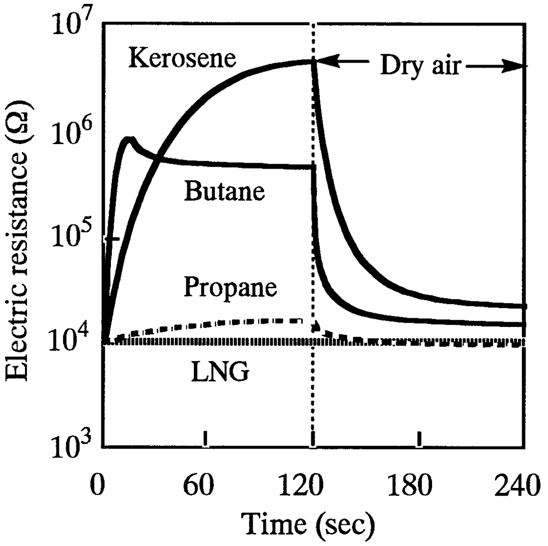


Fig. 5 Effect of various vapor on the electric resistance of composite prepared from PE-grafted carbon black

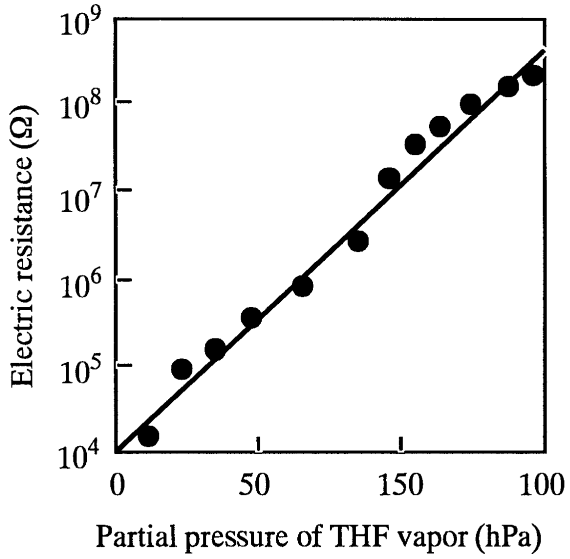


Fig. 6 Relationship between partial vapor pressure of THF vapor and electric resistance of composite prepared from PE-grafted carbon black

Conclusions

1. Crystalline polymers, such as PCL, PEA, and PE, were successfully grafted onto carbon black surface by direct condensation of surface carboxyl groups with terminal functional groups of these polymers.
2. The electric resistance of these crystalline polymer-grafted carbon blacks extremely increased in vapor of good solvent for grafted chain and returned immediately to initial resistance when it was transferred in dry air.
3. The logarithm of electric resistance of the composite from PE-grafted carbon black is linearly proportional to partial pressure of THF vapor.

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