Polymer Bulletin 39, 217–224 (1997)

Polymer Bulletin

Responsibility of electric resistance of polyethyleneimine-grafted carbon black against alcohol vapor and humidity

Norio Tsubokawa[1], **Sachio Yoshikawa**[2], **Kiyotaka Maruyama**[2], **Tomoaki Ogasawara**[2], **Kazuhiro Saitoh**[3]

[1] Department of Material Science and Technology, Faculty of Engineering,
Niigata University, 8050, Ikarashi 2-nocho, Niigata 950-21, Japan
[2] Graduate School of Science and Technology, Niigata University, 8050, Ikarashi 2-nocho,
Niigata 950-21, Japan
[3] Daito Communication Apparatus Co., Ltd, 1-32-15, Oyamadai Shinagawa-ku,
Tokyo 142, Japan

Received: 11 April 1997/Revised version: 16 June 1997/Accepted: 23 June 1997

Summary

Crystalline polyethyleneimine (PEI(C)) was successfully grafted onto carbon black surface by direct condensation of imino groups of PEI with carboxyl groups on the surface using *N,N'*-dicyclohexylcarbodiimide as a condensing agent. The electric resistance of a composite prepared from PEI(C) and PEI(C)-grafted carbon black drastically increased to 10^3-10^4 times of initial resistance in methanol, ethanol, and water vapor. But the change of electric resistance of the composite hardly observed in hexane and toluene vapor. These results suggest the possibility of detection of a slight change of crystalline structure of PEI by the absorption of solvent as a large increase of electric resistance of the composite.

Introduction

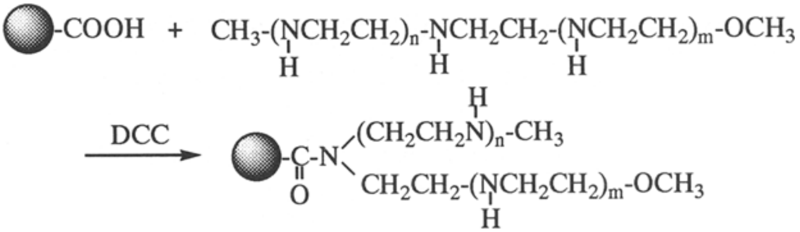
We have reported the grafting of various vinyl polymers onto carbon black surface by the polymerization of vinyl monomers initiated by initiating groups, such as azo or peroxyester, potassium carboxylate, and acylium perchlorate groups, introduced onto the surface (1-3). In addition, the grafting of polymers onto carbon black surface was 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 (4,5). The polymer-grafted carbon blacks thus obtained were easily and uniformly dispersed in polymer matrices (1-3).

It is well known that a composite from vinyl polymer-grafted carbon black-polymer composite, which was crosslinked with a variety of crosslinking agents, shows a large positive temperature coefficient of electric resistance, *i.e.*, PTC, at near the glass transition temperature of the matrix polymer (6,7). That is, the electric resistance of the composite gradually increases with increasing temperature of the composite. This is considered to be due to a widening of the gaps between the carbon black particles by thermal expansion of polymer matrix.

Meyer have reported the stability of the composite of carbon black with crystalline polymer, high-density polyethylene, as PTC resistors (8,9). Recently, we have achieved the grafting of crystalline polymers, such as polyethylene glycol and polyethylene adipate, onto carbon black surface by the direct condensation of surface carboxyl groups with terminal hydroxyl groups of these crystalline polymers using *N,N'*-dicyclohexylcarbodiimide (DCC) as a condensing agent. Furthermore, we pointed out that the electric resistance of the composites prepared from these 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 (10,11). This may be be due to a widening of the gaps between the carbon black particles by melting of crystalline polymer matrix.

Therefore, it is expected that the electric resistance of composite prepared from crystalline polymer-grafted carbon black affected by the absorption of vapor of good solvent of matrix polymer, because of the changing of the gaps between carbon black particles based on the absorption of vapor.

Therefore, in the present paper, the grafting of crystalline polyethyleneimine (PEI(C)) onto carbon black surface (Scheme 1) and the responsiveness of electric resistance of the composite prepared from PEI(C) and PEI(C)-grafted carbon black against alcohol vapor and humidity were investigated.



Scheme 1 Grafting of PEI onto carbon black surface by direct condensation of carboxyl groups with PEI(C) in the presence of DCC

Experimental

Materials

Conductive carbon black used was furnace black, Porousblack, obtained from Asahi Carbon Co. Ltd., Japan. The properties of the carbon black was shown in Table 1. The content of carboxyl (COOH) and phenolic hydroxyl (OH) groups was determined by use of sodium bicarbonate (12) and 2,2-diphenyl-1-picrylhydrazyl (13), respectively. The carbon black was dried *in vacuo* at 110°C for 48 h before use.

2-Methyl-2-oxazoline obtained from Aldrich Chemical Co. Inc. was dried over calcium hydride and distilled 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) and other solvents were purified by ordinary methods.

Polyethyleneimine (PEI)

PEI(C) (Mn=5.0x10^3) was prepared by the hydrolysis of poly(2-methyl-2-oxazoline), which was prepared by cationic ring-opening polymerization of 2-methyl-2-oxazoline using methyl p-toluenesurfonate as a catalyst, according to the method of

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

Saegusa et al.(14). Amorphous PEI (PEI(A)) ($Mn=1.8\text{x}10^3$ and $3.0\text{x}10^4$), which was prepared by cationic ring-opening polymerization of ethyleneimine, was obtained from Nippon Shokubai Co. Ltd., Japan. It was dried *in vacuo* at 80°C for 48 h before use.

Introduction carboxyl groups onto carbon black surface

The introduction of carboxyl groups onto carbon black surface was achieved by the treatment with ACPA (15). Into a flask, 5.0 g of carbon black, 0.5 g of ACPA, and 100 ml of THF were charged and the mixture was stirred with a magnetic stirrer under nitrogen at 70°C for 48 h. After the reaction, the mixture was centrifuged at $1.5\text{x}10^4$ rpm and the supernatant solution was removed by decantation. The resulting carbon black was dispersed in THF and the dispersion was centrifuged again. The procedures were repeated until no more ACPA could be detected in the supernatant solution. The carbon black was dried *in vacuo* at 45°C and stored in a desiccator. The content of carboxyl groups was determined by titration (12).

Grafting of PEI onto carbon black surface

The grafting of PEI onto carbon black surface was achieved by the direct condensation of carboxyl groups on the surface with amino or imino groups of PEI using DCC as a condensing agent (4). Into a flask, 0.25 g of carbon black treated with ACPA, 1.0 g of PEI, 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 $1.5\text{x}10^4$ rpm and the supernatant solution was removed by decantation. The resulting carbon black was dispersed in methanol and the dispersion was centrifuged again. The procedures were repeated until no more PEI could be detected in the supernatant solution.

The percentage of grafting was determined by the following equation.

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

where A is weight of PEI grafted and B is weight of carbon black charged: the quantity of grafted PEI, A, was estimated from the weight of carbon black after grafting reaction minus that before grafting reaction.

Preparation of composite resistor from PEI and PEI-grafted carbon black

The preparation of composite resistor from PEI and PEI-grafted carbon black was carried out as follows. Into a test tube, 0.25 g of PEI grafted carbon black was dispersed in a small amount of THF and 1.00 g of PEI was added. The mixture was stirred with a magnetic stirrer at room temperature to produce a paste of the composite. When untreated carbon black was used, the mixing with PEI was conducted under ultrasonic irradiation, because untreated carbon black was hardly dispersed uniformly in polymer.

Measurement of electric resistance

The measurement of electric resistance of composite resistor was carried out as follows. The composite paste prepared by the above method was coated onto a comb-like electrode, which was prepared by the screen printing of conductive Ag / Pd paste onto a

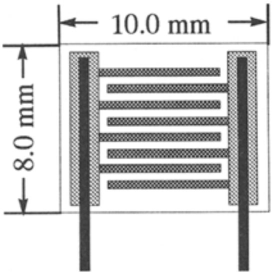


Fig. 1 Comb-like electrode used for the measurement of electric resistance

ceramic plate. The comb-like electrode used in this study was shown in Figure 1.

The electric resistance under alcohol vapor and humidity was measured by hanging the composite resistor in a glass container containing alcohol or water at the bottom. The electric resistance was measured at 25.0°C by use of a digital malutimeter (Advantest Co. Ltd., Japan: type R6871E-DC).

Results and discussion

Grafting of PEI onto carbon black surface

In the previous paper, we have reported the grafting reaction of surface carboxyl groups with polymers having terminal hydroxyl and amino groups using DCC as a condensing agent (4). Therefore, the grafting of PEI(C) and PEI(A) onto carbon black surface by direct condensation of surface carboxyl groups with amino or imino groups of PEI in the presence of DCC was examined (Scheme 1).

In general, conductive carbon blacks 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 (15). 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 PEI grafting onto carbon black surface. In the absence of DCC, the grafting of PEI onto carbon black surface scarcely observed. On the contrary, the grafting of both PEI(C) and PEI(A) successfully proceeded in the presence of DCC as a condensing agent. Percentage of grafting of PEI(A) was larger than that of PEI(C); especially, percentage of high molecular weight PEI(A) exceeded 50%. But the mole number of grafted PEI(A) chain on 1.0 g of carbon black (μmol/g) decreased with increasing molecular weight, because of steric hindrance of carbon black surface.

The reactivity of PEI(C) was lower than that of PEI(A). This may be due to the fact that the solubility of PEI(A) in THF is higher than that of PEI(C) and PEI(A) has much terminal amino groups.

No gelation during the above grafting reaction was observed. This may be due to the fact that a large excess of PEI is reacted with surface carboxyl groups on carbon black. The same tendency was reported in the reaction of functional polymers with surface functional groups on carbon black (4,5,16).

By the grafting of PEI, the carbon black surface changed from hydrophilic to extremely hydrophilic. In addition, both PEI(C)-grafted and PEI(A)-grafted carbon blacks readily and uniformly dispersed in solvents, such as methanol, ethanol, and water, and PEI matrix.

Electric resistance of composite resistor from PEI-grafted carbon black

Table 3 shows the electric resistance of composite resistor prepared from PEI and PEI-grafted carbon black under dry air and methanol vapor. The electric resistance of composite prepared from PEI(C) and untreated carbon black was also shown in Table 3.

Table 2 Grafting of PEI onto carbon black surface

PEI grafted	*Mn* x 10^{-3}	DCC (mg)	Grafting (%)	Grafted polymer (μmol/g)
Crystalline	5.0	-	3.2	6.4
Crystalline	5.0	25	7.1	14.2
Amorphous	1.8	25	11.3	62.8
Amorphous	30	25	50.7	16.9

Carbon black, 0.25 g; PEI, 1.0 g; THF, 20.0 ml; 60°C; 48 h.

Table 3 Electric resistance of composites from PEI and PEI-grafted carbon black in dry air and methanol vapor

Composite	*Mn* x 10^{-3}	Electric resistance (Ω)	
		Dry air	MeOH vapor
PEI(C) + Ungrafted CB	5.0	150k	140k
PEI(C) + PEI(C)-grafted CB	5.0	20	10k
PEI(A) + PEI(A)-grafted CB	1.8	400k	320k
PEI(A) + PEI(A)-grafted CB	30	2000k	1800k

Measuring temperature, 25.0°C.

It is interesting to note that the electric resistance of composite prepared from PEI(C) and PEI(C)-grafted carbon black was much smaller than that of amorphous one.

On the other hand, even if PEI(C) was used, the electric resistance of composite from untreated carbon black was also larger than that from PEI(C)-grafted one. This may be due to the presence of aggregates of carbon black particles in the composite, because untreated carbon black hardly dispersed uniformly in PEI.

In addition, the electric resistance of composites from PEI(C) and PEI(C)-grafted carbon black in methanol vapor at 25°C drastically increased from 20Ω to 10 kΩ. But the electric resistance of composite from PEI(A) and untreated carbon black scarcely varied: the resistance tends to decrease in methanol vapor.

Effect of various vapor on the electric resistance of composite from PEI(C) and PEI(C)-grafted carbon black

Figure 2 shows the effect of of various vapor on the electric resistance of composite from PEI(C) and PEI(C)-grafted carbon black at 25°C. It is interesting to note that the electric resistance of the composite drastically increased in methanol, ethanol, and water vapor, which are good solvent for PEI. On the contrary, the electric resistance hardly changed in toluene and hexane, which are non solvent of PEI.

This is due to a slight change of gaps between carbon black particles based on the absorption of vapor of good solvent by PEI(C). These results suggests the possibility of

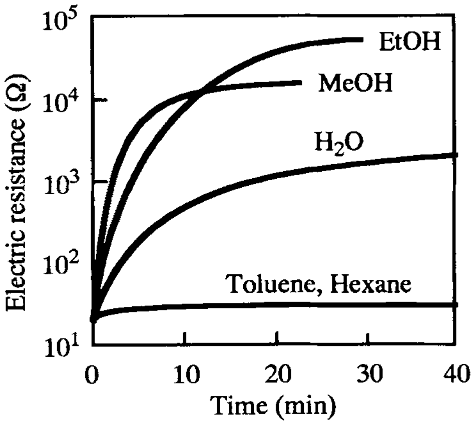


Fig. 2 Effect of various vapor on the electric resistance of composite prepared from PEI(C) and PEI(C)-grafted carbon black

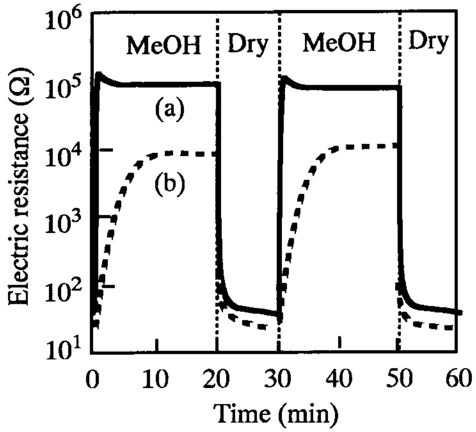


Fig. 3 Effect of composition of composite of PEI(C) and PEI(C)-grafted carbon black on the responsiveness to methanol vapor

Carbon black content; (a) 10wt%, (b) 20wt%.

detection of a slight change of crystalline structure of PEI by the absorption of solvent as a large change of electric resistance of the composite.

Effect of composition of PEI(C) and PEI(C)-grafted carbon black on the responsiveness

The effect of composition of PEI(C) and PEI(C)-grafted carbon black on the responsiveness to methanol vapor was examined. The results are shown in Figure 3. By decreasing content of carbon black from 20wt% to 10wt%, the initial resistance increased, but the responsiveness to methanol vapor extremely increased.

In addition, Figure 3 shows that the electric resistance of these composite returns immediately to initial resistance when the composite is transferred in dry air. The responsiveness of electric resistance were reproducible even after 30 times cycle of exposure to methanol vapor and dry air.

Relationship between electric resistance of the composite and relative humidity

Figure 4 shows the relationship between electric resistance of the composite and relative humidity. It became apparent that the logarithm of electric resistance is linearly proportional to relative humidity. This indicates that the composite can be applied as a humidity sensor.

Relationship between electric resistance of the composite and partial pressure of methanol in mixture of water and methanol vapor

The relationship between electric resistance of the composite and partial pressure of methanol in mixture of water and methanol vapor in air was examined under atmospheric pressure at 25°C. The result is shown in Figure 5. It was found that the logarithm of electric resistance is also linearly proportional to partial pressure of methanol in the mixture vapor. This indicates that the composite can be also applied as a novel sensor of alcohol vapor.

Conclusions

PEI(C) was successfully grafted onto carbon black surface by direct condensation of surface carboxyl groups with PEI(C). The electric resistance of composite from PEI(C) and PEI(C)-grafted carbon black extremely increased in alcohol vapor and humidity and the electric resistance returned immediately to initial resistance when it was transferred in dry air. The logarithm of electric resistance is linearly proportional to relative humidity and partial pressure of methanol. This indicates that the composite can be applied as a novel sensor for humidity and alcohol vapor.

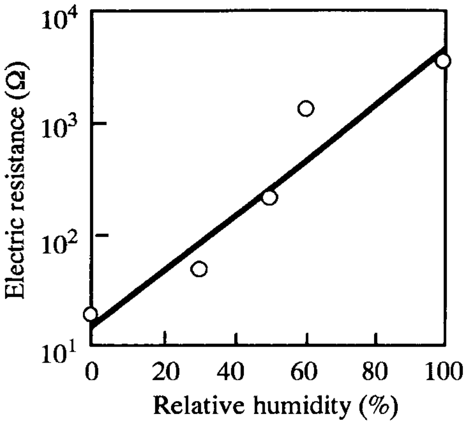


Fig. 4 Effect of relative humidity on the electric resistance of composite prepared from PEI(C) and PEI(C)-grafted carbon black

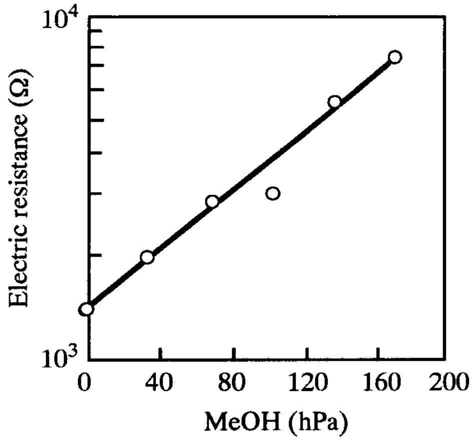


Fig. 5 Effect of partial pressure of methanol vapor on the electric resistance of composite prepared from PEI(C) and PEI(C)-grafted carbon black

The mechanism of the responsiveness of the composite to alcohol vapor and humidity and the responsiveness of the composite from other crystalline polymer to various vapor are now under investigation.

Acknowledgement

This study was partly supported by a Grant-in-Aid for Scientific Research (C) (No.08650795) from Ministry of Education, Science, Sports and Culture of Japan.

References

1) Tsubokawa N (1992) Prog Polym Sci 17: 417.
2) Tsubokawa N (1996) Kobunshi (High Polymer) 45: 412.
3) Tsubokawa N (1996) Carbon Black (Graft Copolymers). In: Salamone JC (ed) Polymer Materials Encyclopedia. CRC Press New York (vol.2, pp941-946).
4) Tsubokawa N, Hosoya M, Kurumada J (1995) Reactive Functional Polym 27: 75.
5) Tsubokawa N, Kurumada J (1996) J Jpn Soc Color Material (SHIKIZAI) 69: 90.
6) Frydman E (1945) UK Patent Specification 604,695.
7) Ohkita K, Fukushima K (1969) Japan Plastics 3 (3): 6; ibid 3 (4):25.
8) Wargotz B, Alvino WM (1967) Polym Eng Sci 7: 63.

9) Meyer J (1974) Polym Eng Sci 14: 706.
10) Ueno A, Sugaya S (1994) Preprints 3rd Symposium on Intelligent Materials: 107.
11) Tsubokawa N, Maruyama K, Ogasawara T, Koshiba M (1996) Polym Preprints, Jpn 45: 2856.
12) Rivin D (1963) Rubber Chem Technol 36: 729.
13) Ohkita K, Tsubokawa N (1972) Carbon 10: 631.
14) Saegusa T, Ikeda H, Fujii H (1972) Macromolecules 5: 108.
15) Tsubokawa N, Magara K, Sone Y (1989) Nippon Gomu Kyokaishi 62: 668.
16) Tsubokawa N (1993) Nippon Kagaku Kaishi : 1012.