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Novel vapor sensor from polymer-grafted carbon black: effects of heat-treatment and γ-ray radiation-treatment on the response of sensor material in cyclohexane vapor

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Abstract

Polyethylene (PE) was grafted onto carbon black surface by γ-ray radiation of the PE-adsorbed carbon black. Vapor sensor composite materials were prepared from the PE-grafted carbon black and PE as a matrix polymer. The effects of heat-treatment and γ-ray radiation-treatment on the response of the electric resistance of the sensor material against cyclohexane vapor were investigated. The heat-treatment of the composite improved the crystallinity of the matrix PE, and thus increased the responsiveness against cyclohexane vapor about five times that of the untreated one. The γ-ray radiation-treatment slightly decreased the responsiveness against cyclohexane vapor, because the γ-ray radiation-treatment induced the crosslinking of PE. On the contrary, the stability and reproducibility of the vapor sensor material remarkably improved. By the heat-treatment followed by the γ-ray radiation-treatment, a novel stable and reproducible sensor material was obtained, which allowed to identify and to quantify certain vapors in air accurately. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Carbon black; γ-Ray radiation grafting; Vapor sensor

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1. Introduction

The gas sensor and vapor sensor material based on a conducting polymer [1–4], a polymer electrolyte [5,6] and a polymer/carbon black composite [7–19] has been studied intensively due to its easy fabrication with a low-cost, high rapid response rate and sensitivity to the targets.

In a previous paper, we have reported that the electric resistance of a composite prepared from low-polar crystalline polymer-grafted carbon black, such as PE-grafted carbon black, dramatically increased with several orders of magnitude when it was exposed in a non-polar or low-polar solvent vapor like cyclohexane, tetrachloride, toluene, hexane and tetrahydrofuran (THF), but the electric resistance hardly changed in a polar solvent vapor, such as water and alcohols [13,14].

On the other hand, the electric resistance of a composite with a polar crystalline polymer-grafted carbon black, such as poly(ethylene oxide)-grafted carbon black, increased drastically in polar solvent vapor, but had hardly any response to non- and low-polar solvent vapor [15,16]. Therefore, these sensor materials from crystalline polymer-grafted carbon black were possible to examine and identify solvent vapors in air at room temperature under normal atmosphere [7–19] and chemical compounds in solvent [20].

It was considered that the crystallinity of the matrix polymers played an important role in the response of the sensor materials [18]. That is, the crystallinity change of the crystalline polymer by absorbing solvent vapors was the main reason to cause the response. In dry air, carbon black was considered to be dispersed only in the amorphous regions of the matrix crystalline polymer [21–24]. When the sensor material absorbed solvent vapor, the crystalline polymer was dissolved and cut the carbon black/amorphous polymer continuous phase and/or the carbon black network in the amorphous phase, leading to a large change of electric resistance of the sensor material [18].

In addition, the effects of the addition of crystalline organic compound, such as *N*,*N*′-dicyclohexylcarbodiimide (DCC), on the responsiveness of the sensor material from PE and PE-grafted carbon black has been reported [18]. It was found that by the addition of DCC to a composite from

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PE and PE-grafted carbon black the responsiveness was remarkably improved to THF vapor.

In the above polymer/carbon black sensor materials, it was often observed that the electric resistance decreased slowly in the good solvent vapor after reaching to the maximum resistance, which presents a negative vapor coefficient (NVC) [16]. Similar to the negative temperature coefficient (NTC, the decrease of electric resistance of the polymer/carbon black composite above the melting temperature of the polymer), NVC was due to the movement of carbon black when the crystalline polymer was melted. That is, the carbon black was re-distributed when the crystalline polymer melted and the viscosity decreased, and a weak carbon black network was formed, resulting in a slight decrease of the electric resistance.

In our previous paper [19], we designed a simple method to graft PE onto the carbon black surface by γ-ray irradiation of the PE-adsorbed carbon black directly. We have reported that the electric resistance of the sensor material prepared from PE-grafted carbon black and PE in cyclohexane vapor drastically increased 10^3–10^4 times the initial resistance, showing a good sensing property.

In this study, to improve the responsiveness, the stability and the reproducibility of the sensor material, the effects of heat-treatment and γ-rays radiation-treatment of the sensor material from PE and PE-grafted carbon black will be investigated in detail.

2. Experimental

2.1. Materials and reagents

Conductive carbon black, Asahi 60 H, was used as the surface. It is a furnace black made by Asahi Carbon Co. Ltd (Niigata, Japan). The specific surface area of the carbon black is 60 m^2/g, and the particle size is 41 nm. The carbon black was dried in a vacuum at 110 °C for 48 h before use.

Polyethylene (PE), a linear lower density type, was purchased from Aldrich Chemical Co., and was used as received. The weight and number average molecular weight of the PE is 1.3×10^5 and 2.5×10^4, respectively. It is copolymerized with 5–10 wt% hexene; the melt index is 100 g/10 min (190 °C/2.16 kg, ASTM D 1238) and the density is 0.929 g/ml. Analytical grade *m*-xylene and cyclohexane, pursed from Wako Pure Chemical Ind. Ltd, Japan, was used without any further purification.

2.2. γ-Ray radiation grafting of PE onto carbon black surface

The γ-ray radiation grafting of PE onto carbon black surface was achieved by a two-step method [19]. That is, the PE was first adsorbed onto carbon black surface through *m*-xylene solution; then, the PE-adsorbed carbon black was irradiated at a dose rate of 20 kGy/h up to 300 kGy at 120 °C in nitrogen. The PE-grafted carbon black, with PE grafting of 10.3 wt%, estimated by TGA (Shimadzu TGA-50, Japan), was used as the conducting particles, because the higher grafting of PE than 15 wt% onto the surface results in drastic decrease in the conductivity of the carbon black itself. The detail of the grafting procedures and TGA measurement was described in the previous paper [19].

2.3. Sensor material and response measurement

The sensor material was prepared from PE-grafted carbon black and PE. In the PE/carbon black conductive material, the carbon black content is 20 wt%. The PE/carbon black composite was coated onto a ceramic plate equipped with Pd/Ag electrode. The DC electric resistance of the electrode was recorded by an ohmmeter at 30 °C every 10 s in dry air and then in saturated cyclohexane vapor at 30 °C. The details of the preparation of the sensor material, the measurement of electric resistance and the response analysis were described in our previous papers [14–18].

2.4. Heat-treatment and γ-ray radiation-treatment

Heat-treatment of the sensor material was performed as follows: the sensor material was first put into an oven at 170 °C for 10 min, then quickly transferred to an oven at the temperature of 25, 80, 100, 120 °C for 10 h, or at 140, 160 °C for 2 h. After these heat-treatments, the sensor material was stored in a desiccator at room temperature for a long time over 48 h before use.

γ-Ray radiation-treatment was carried out using a ^{60}Co γ-ray radiation at a dose rate of 10 kGy/h in atmosphere. The irradiation dose of the sensor material is 30, 60, 90, and 300 kGy. After irradiation, the sensor material was stored in the same method described earlier.

3. Results and discussion

3.1. Effect of heat-treatment

The conductive composite prepared from a crystalline polymer and polymer-grafted conductive carbon black had a unique feature of electric resistance response when the composite was exposed in an organic solvent vapor [13–18]. Therefore, we have pointed out that the composite from polymer-grafted carbon black is used as a novel sensor material. On the other hand, we have reported the γ-ray radiation grafting of PE onto carbon black and the property for the conductive composite of PE-grafted carbon black and PE as a vapor sensor [19].

In this study, a more exploring investigation was conducted to improve the properties of the electric resistance response of the vapor sensor material. The influences of heat-treatment and γ-ray radiation-treatment on the response of the vapor sensor material to cyclohexane vapor was investigated in detail.

Fig. 1 shows the effect of heat-treatment at 100, 120, 140,

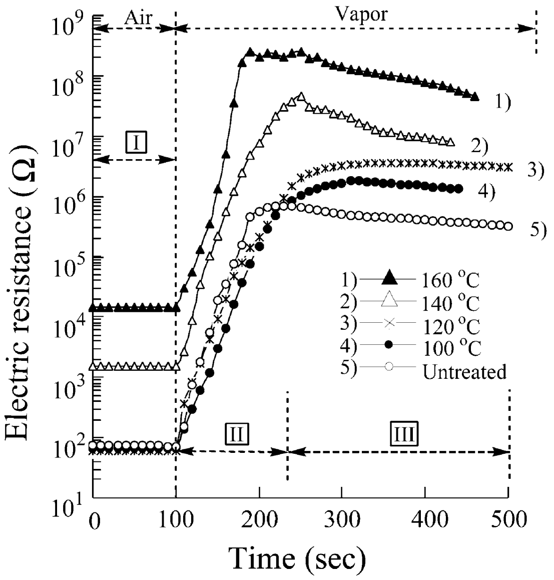

Fig. 1. Effects of the heat-treatment temperature of the sensor materials on the electric resistance in dry air and in cyclohexane vapor at 30 °C.

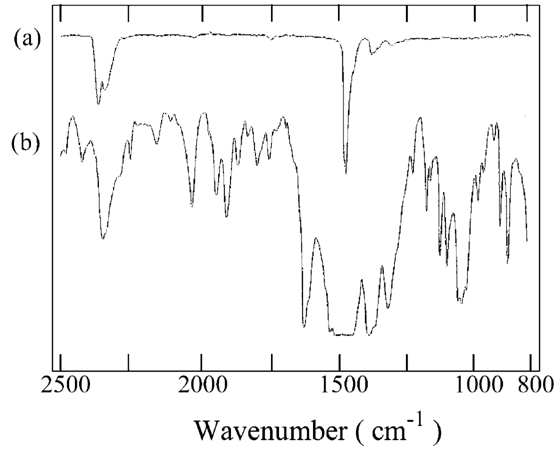

Fig. 2. Infrared spectrum of PE film (a) before and (b) after heat-treatment at 160 °C.

and 160 °C on the electric resistance of the sensor materials in dry air (for 100 s) and in saturated cyclohexane vapor (after 100 s) at 30 °C. The results of the electric resistance of the sensor material without heat-treatment are also shown. The curves of the electric resistance showed three distinct regions as shown in Fig. 1: (I) the initial resistance (R_0) in dry air, (II) the drastic increase region of the electric resistance just after the transition of sensor material from dry air to cyclohexane vapor, and (III) the steady state electric resistance in cyclohexane vapor.

The results of heat-treatment at 100 and 120 °C showed slight effect on the initial electric resistance (R_0) of the sensor material in dry air. That is, the initial resistance of the sensor material without heat-treatment is 73 Ω, and the initial resistance of the sensor material after the heat-treatment at 100 and 120 °C is 67 and 60 Ω, respectively. It is interesting to note that when the sensor material was heated at 140 and 160 °C, the initial resistances drastically increase to 1600 and 14,500 Ω, respectively. The slight decrease of the initial resistances of the sensor material treated at 100 and 120 °C may be due to the increase in crystallinity of the matrix polymer [24–27].

The drastic increase in initial resistance of the sensor material treated at 140 and 160 °C was not in agreement with the results reported by Sumita et al. [28] and Bin et al. [29], where the resistance generally decreased due to the carbon black re-aggregation during the heat-treatment above the melting point. In our experiment, the heat-treatment time at 140 and 160 °C in air is 2 h, which is very longer than that reported in the earlier papers. By the longer heat-treatment in air, the properties of PE are considered to be changed.

Fig. 2 shows the infrared spectra of PE film (a) before and (b) after heat-treatment at 160 °C. As shown in Fig. 2, many peaks were newly appeared after heating, indicating that a complicated reaction proceeds. Therefore, the drastic increase in initial resistance of the sensor material treated at 140 and 160 °C may be due to the decrease in crystallinity and the oxidation/degradation of the matrix polymer (PE) at the high temperature in air.

When the sensor material was transferred from dry air in cyclohexane vapor, all of the curves showed a linear logarithmic increase of electric resistance with almost the same slope (see Fig. 1, region (II)). Therefore, the heat-treatment of the sensor material scarcely has influence on the response rate to the cyclohexane vapor.

In the steady state of electric resistance in the cyclohexane vapor (see Fig. 1, region (III)), it is clear that the maximum electric resistance (R) increases with the increase of temperature of the heat-treatment.

The responsiveness is evaluated as R/R_0, where R is the maximum electric resistance in cyclohexane vapor, and R_0 is the electric resistance in dry air. The effects of heat-treatment temperature on the initial resistance (R_0) and on the responsiveness (R/R_0) to cyclohexane vapor are shown in Fig. 3(a) and (b), respectively. The blank triangle and filled triangle show the average of initial electric resistance and responsiveness, respectively. The error bars are also shown in Fig. 3(a) and (b).

When the sensor material was heated below 120 °C, the initial resistances of the sensor material are very stable, and the scatter of the initial electric resistances of five samples are negligibly small as shown in Fig. 3(a) by error bar; the initial resistance decreases slightly with the increase of the heat-treatment temperature. On the contrary, by the heat-treatment above 120 °C, the initial resistance of the sensor material drastically increased and was very unstable, the initial electric resistances of five samples are varied from 10^2 to 10^3 Ω by the heat-treatment at 140 °C, and from 10^3 to 10^5 Ω by the heat-treatment at 160 °C, as shown in Fig. 3(a).

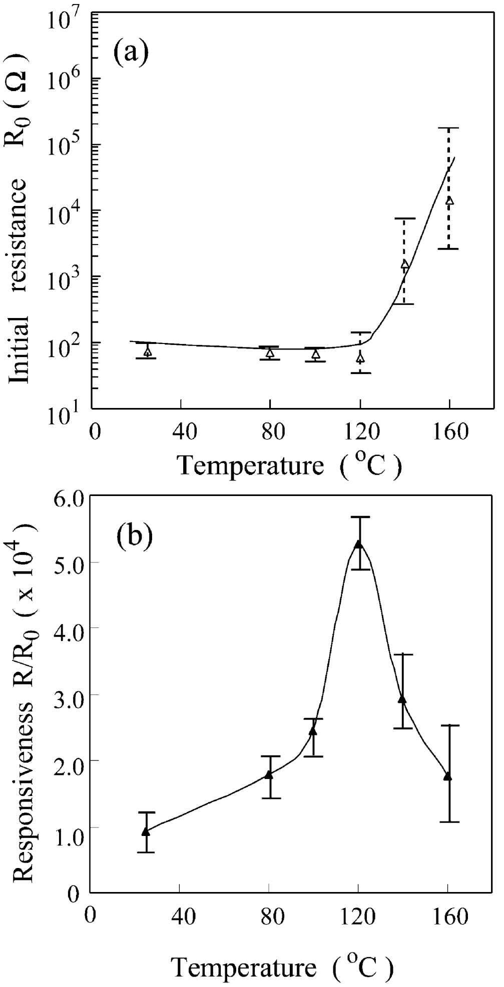

Fig. 3. Effects of the heat-treatment temperature of the sensor materials on (a) the initial resistance (in dry air) and (b) the responsiveness to the cyclohexane vapor at 30 °C.

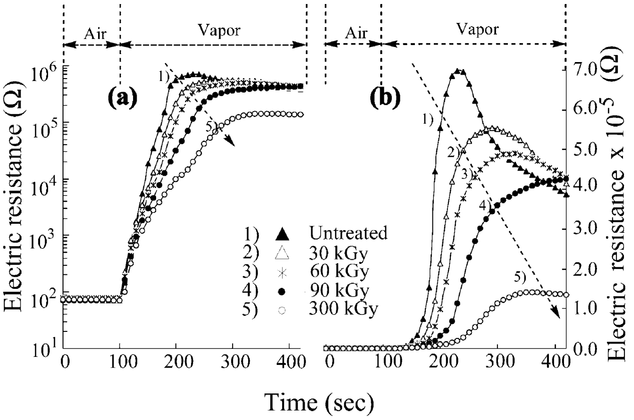

Fig. 4. Effects of γ-ray radiation-treatment of the sensor materials on the response to the cyclohexane vapor at 30 °C. The ordinate of electric resistance of (a) is logarithmic and (b) is linear type.

The effects of heat-treatment temperature on the responsiveness of the sensor material to cyclohexane vapor show similar tendency as that of the initial resistance as shown in Fig. 3(b). However, by heat-treatment below 120 °C, the responsiveness increases with the increase of heat-treatment temperature, and the scatter of the responsiveness of the five samples is relatively small. By the heat-treatment at 120 °C, the responsiveness reaches its maximum. On the contrary, by the heat-treatment above 120 °C, the responsiveness decreases, and the scatter of the responsiveness of the five samples becomes very large. This may be due to the instability of initial resistance, and the changing of chemical properties of the sensor material by heat-treatment.

3.2. *Effect of γ-ray irradiation*

Generally, the drastic increase in resistance of carbon black/polymer composite near the melting point of polymer is described by a positive temperature coefficient (PTC), whereas a decrease of resistance above the melting point is described by a negative temperature coefficient (NTC) [29]. Similar to NTC, both before and after the heat-treatment, as shown in Fig. 1, the NVC is also observed. That is, the electric resistance of the sensor material decreased after reaching the maximum resistance in cyclohexane vapor.

To decrease or eliminate the NVC characteristic, γ-ray radiation-treatment of the sensor material was performed. Fig. 4 shows the effect of γ-ray radiation-treatment of the sensor material on the electric resistance in dry air and in cyclohexane vapor. The ordinate of Fig. 4(a) is logarithmic electric resistance, while Fig. 4(b) is linear electric resistance.

The γ-ray radiation-treatment up to 300 kGy seems to show no effects on the initial resistance of the sensor material. However, in cyclohexane vapor, the maximum value of the electric resistance of the sensor material decreases with the increase of the irradiation dose. The time to reach the maximum electric resistance increased with the increase of the irradiation dose. Therefore, it is concluded that the γ-ray radiation-treatment considerably decreases the responsiveness (R/R_0) and the response rate of the sensor material to cyclohexane vapor.

Though the responsiveness and response rate of the sensor material to cyclohexane vapor are slightly sacrificed, the γ-ray radiation-treatment is of very benefit to the practical application of the sensor material. The reason is as follows. Without the γ-ray radiation-treatment, as shown in Fig. 4(b) (curve (1)), the electric resistance of the sensor material in cyclohexane vapor decreases after reaching to the maximum value, resulting in an unstable response of the sensor material, which is the fatal defect to identify and quantify a solvent vapor.

By γ-ray radiation of 30 and 60 kGy, the electric resistance after reaching to the maximum value slowly decreased. By γ-ray radiation of 90 kGy, there is no decrease of electric resistance of the sensor material in cyclohexane vapor after reaching to the maximum value,

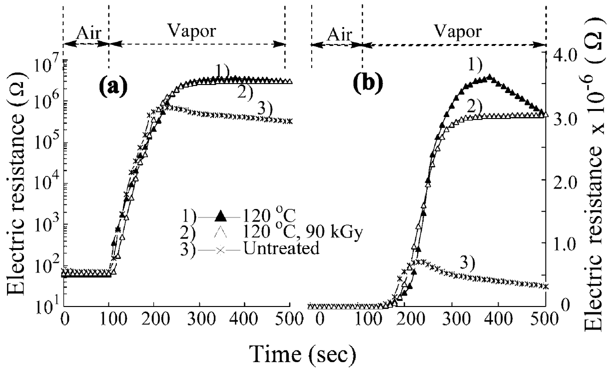

Fig. 5. Response of the electric resistance of the sensor materials. (1) Heat-treated at 120 °C, (2) heat-treatment at 120 °C followed by γ-ray radiation, and (3) untreated.

and the electric resistance reaches its steady state value after 400 s. On the contrary, with more γ-ray radiation-treatment, such as 300 kGy, the response of the sensor material to cyclohexane is very stable, but the responsiveness decreased largely.

Therefore, optimum irradiation dose for the sensor material is about 90 kGy in atmosphere. The stable response of the sensor material is due to the partial inhibition of moving of carbon black particles in the composite by γ-radiation crosslinking of PE chain [27,30–32]. The decrease of responsiveness of the sensor material is caused by the decrease of crystallinity of the matrix polymer at high dose of γ-ray irradiation [27,30–32].

3.3. *Effect of heat-treatment followed by γ-ray radiation*

From the results obtained earlier, the optimum heat-treatment and γ-ray radiation-treatment of sensor material are 120 °C and 90 kGy, respectively. The heat-treatment increases the responsiveness, while the γ-ray radiation-treatment increases the stability of the response with slightly sacrificing the responsiveness and the response rate of the sensor material to cyclohexane vapor. Therefore, it is expected that an ideal sensor material can be obtained by heat-treatment and γ-ray radiation-treatment in turn/or simultaneously.

The response of sensor material treated at 120 °C and then treated with irradiation dose of 90 kGy to cyclohexane vapor was shown in Fig. 5 (curve (2)). The ordinate of Fig. 5(a) is logarithmic electric resistance while Fig. 5(b) is linear electric resistance. To comparison, the response results of the untreated sensor material (curve (3)) and only heat-treated sensor material at 120 °C (curve (1)) to cyclohexane vapor are also plotted. It was found that the untreated sensor material (curve 3) shows a smallest responsiveness. The 120 °C heat-treated sensor material (curve 1) shows the highest responsiveness, but the electric resistance and the response in cyclohexane vapor is considerably unstable. On the other hand, the sensor materials heat-treated at 120 °C and then γ-ray radiation of 90 kGy shows a relative higher responsiveness and a most stable response to the cyclohexane vapor.

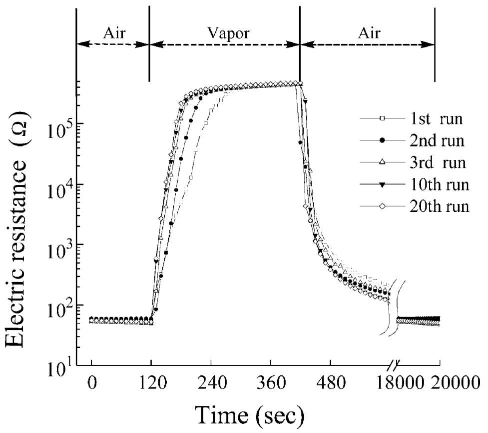

Fig. 6. Reproducibility of the response of electric resistance response of sensor material heat-treated at 120 °C followed by γ-ray radiation.

Fig. 6 shows the reproducibility of the electric resistance response of the sensor material heat-treated at 120 °C and then γ-ray radiation of 90 kGy to cyclohexane vapor. The electric resistance of the sensor material not only increases drastically in cyclohexane vapor, but also returns quickly to its initial resistance when the sensor material is transferred to dry air.

The resistance change of the sensor material is reversible, and the response of the electric resistance is excellently reproducible in every cycle of exposure to cyclohexane vapor and dry air. In addition, the response rate of the second run is rapider than that of the first run, and that of third run is rapider than that of the second run. After third run, the response rate shows no change up to 20th run. During the circle-run detection, both the change of the initial resistance of the sensor material in dry air and the maximum resistance in cyclohexane vapor are less than 10%.

On the other hand, as shown in Fig. 7, the reproducibility of the electric resistance response of the sensor material from PE and PE-grafted carbon black without heat-treatment and γ-ray radiation-treatment is not so good in comparison with that with heat-treatment and γ-ray radiation as shown in Fig. 6. The initial resistance of the sensor material in dry air is varied from 62 (first run) to 88 Ω (20th run), and the maximum resistance in cyclohexane vapor is varied from 160,000 (1st run) to 240,000 Ω (20th run), showing a large change during the circle-run detection.

The response of the electric resistance is considered to be caused by the structure change of sensor material by the absorption and desorption of the organic solvent vapor [13–18]. It has been reported that the crystallinity of polymer increased by the heat-treatment at or below the melting temperature of matrix polymer [25–27]. The γ-ray radiation-treatment of polymer induced the crosslinking

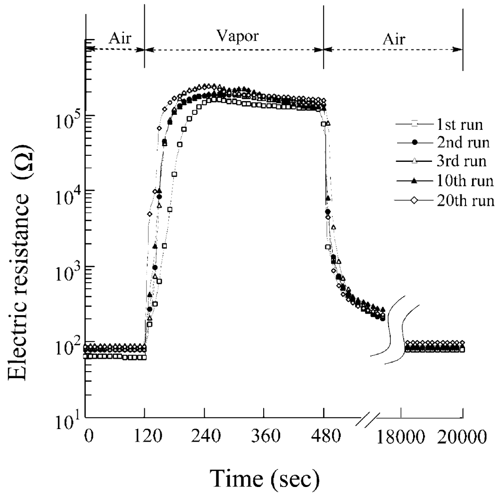

Fig. 7. Reproducibility of the response of electric resistance response of sensor material without heat-treatment and γ-ray radiation-treatment.

[27,30–32]. The former causes the increase of the responsiveness, while the later inhibits the carbon black from re-aggregation in cyclohexane vapor. Therefore, the high grade of sensor material from polymer-grafted carbon black was obtained by the heat-treatment followed by the γ-ray irradiation.

4. Conclusions

1. A novel vapor sensor material was successfully prepared from PE and the PE-grafted carbon black, which was prepared by γ-ray radiation of the PE-adsorbed carbon black at 120 °C in nitrogen.
2. By heat-treatment of the sensor material at 120 °C, the responsiveness of the sensor material increased five times that of untreated one. On the other hand, the electric resistance in cyclohexane vapor was remarkably stabilized by γ-ray radiation-treatment.
3. By the heat-treatment at 120 °C followed by the γ-ray radiation of 90 kGy, a novel stable and reproducible sensor material was obtained, which can identify and quantify cyclohexane vapor in air accurately.

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