

Electrical Properties of Carbon-Black Grafted with Polymers Using an Anionic Catalyst

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Synopsis

The polymer-grafted carbon black (GC) was prepared by an anionic polymerization of methyl methacrylate in the presence of carbon black previously treated with *n*-butyl lithium. The electrical properties of the resistors obtained using the GC material were studied. For a comparison with the above resistors, resistors with a smaller grafting ratio or without grafting were also prepared. It was found that the resistivity increased with an increase of the grafting ratio and that, by comparing resistors with similar resistivities, resistivity variation with temperature was less for higher grafting ratios. The resistors with a resistivity in the range of ca. 10^3 – 10^6 Ω -cm showed a remarkably large positive anomaly, but, for a resistivity larger than 10^7 Ω -cm, the temperature coefficient was negative.

INTRODUCTION

Carbon black-polymer compositions are of interest as conductive materials and have been investigated by many researchers.¹⁻³ Thus, conductive materials have been used for various purposes, such as electric shielding,⁴ prevention of static electricity accumulation,⁵ heating,⁶ etc. At an earlier stage, the application to a heating purpose had considerable difficulties.² When used as a surface heater, it was difficult to obtain uniform conductivity, and the conductive film was liable to overheat due to heat from local sources. Ohkita et al.,^{7,8} who obtained polymer-grafted carbon black (GC) by reacting a vinyl monomer on the surface of carbon black with 2,2'-azobisisobutyronitrile (AIBN) or benzoyl peroxide as a radical initiator, applied GC to a surface heater.⁶ The GC dispersed very well in an appropriate solvent, so that it was possible to make a heater with uniform conductivity all over the surface.

Other authors⁹⁻¹² have also studied the electrical properties of GC for the purpose of developing a resistor device and a surface heater, and demonstrated the electrical properties of the GC conductors crosslinked with a variety of crosslinking agents.

Recently, Ohkita et al.^{13,14} have succeeded in preparing GC materials with higher degrees of grafting using an anionic polymerization procedure. Methyl methacrylate (MMA) was found to react effectively of the surface of carbon black previously treated with *n*-butyl lithium (*n*-BuLi).

This paper demonstrates the electrical properties of GC conductors obtained by grafting MMA on the surface of furnace black previously treated with *n*-BuLi as an initiator.

EXPERIMENTAL

Materials and Reagents. The carbon black used was Philblack O (HAF, N330) from Phillips Chemical Co., obtained through A. A. Chemical Co. This carbon black contained 1.33% of oxygen.^{13,15} The specific surface area and the average diameter were reported to be 79.6 m²/g and 29.4 nm,^{13,15} respectively. The carbon black was kept in the dark in a sealed glass container, and Soxhlet-extracted with benzene and dried at 100°C for 4 h in vacuum prior to use.

MMA monomer and toluene were obtained from Wako Pure Chemical Ind., Ltd., and purified according to the procedure^{13,14} described previously. *n*-BuLi obtained from Wako Pure Chemical Ind., Ltd. was 15% hexane solution, and was sealed in a glass tube in a known quantity.

Polymerizations in the Presence of Carbon Black. The anionic polymerization of MMA in the presence of carbon black was carried out as described previously.^{13,14} Given weights of carbon black and toluene were stirred in a 100-mL flask by a magnetic stirrer at a temperature kept at 0°C. 1 or 2 mL of 15% *n*-BuLi hexane solution were added and reacted for a specified period of time under a nitrogen atmosphere. A given weight of MMA was then added to the reaction mixture, which polymerized at 0°C for a specified period of time under nitrogen with stirring by a magnetic stirrer.

The radical polymerization of MMA in the presence of carbon black was carried out according to the procedure^{7,8} described previously. Nine mL of toluene, 1.5 g of carbon black, 3.0 g of MMA, and 0.06 g of AIBN as an initiator were dissolved and allowed to react for 8 h at 95°C under a nitrogen atmosphere.

The conversion was obtained in the following manner: An excess amount of methyl alcohol was added to the reaction mixture to separate out the carbon black containing the polymer; the carbon black was then washed with methyl alcohol and dried in vacuum. The conversion was calculated from the difference in the weight of this mixture and that of the carbon black initially added. The grafting ratio was obtained by the following procedure: Ca. 0.5 g of the dried carbon black-polymer mixture was accurately weighed and Soxhlet-extracted for 48 h with benzene. The ratio was determined using the following equation:

$$\text{grafting ratio} = \frac{\text{wt after extraction} - \text{wt carbon black}}{\text{wt carbon black}} \times 100 (\%)$$

Here, weight of carbon black contained was determined using the following equation: wt carbon black = wt dried carbon black-polymer mixture used in extraction \times [wt carbon black used in each polymerization/(wt carbon black used in each polymerization + wt monomer used in each polymerization \times conversion/100)] (g).

The Preparation of Resistors. Resistors were prepared according to the procedure^{9,10} described previously. The mixture containing the polymer obtained by polymerization was dispersed in toluene again to be used as a paste. The resistors were made by coating the dispersed paste on rectangular porcelain plates of 18 mm wide with two electrodes placed 18 mm apart, and drying the samples at 60°C for 6 h in a vacuum drying chamber after air drying. A coated film on the porcelain plate was ca. 20–30 μ m thick. The resistor of a mixture without the graft polymerization was made in the following manner: PMMA and carbon black were mixed for 6 h in toluene with glass beads, the paste was

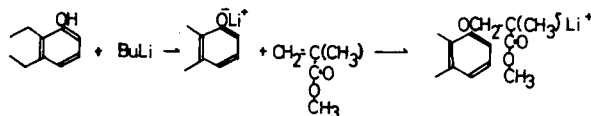


Fig. 1. Reaction scheme.

coated on a porcelain, and the porcelain plate was dried for 6 h at 60°C in a vacuum drying chamber after air drying.

Resistivity. The resistivity of the resistors was measured with a digital voltmeter (Kikusui Electric Industrial Co., Ltd.) by connecting wires to the terminals of the porcelain plate set in a constant electric chamber. The resistance variation with temperature between 40°C and 140°C was observed by raising the temperature at the heating rate 1°C/min. Resistivity larger than $10^6 \Omega\text{-cm}$ were measured with an electrometer (Takeda Riken Industrial Co., Electrometer TR-8651). In this paper, the resistance variation R_t , is presented by $(R_t - R_{40}) \times 100/R_{40}$, where R_t and R_{40} are the resistances at a given temperature t and 40°C, respectively.

Molecular Weight. For the homopolymer separated from the polymerization product mixture, the molecular weight was measured with the viscosity method.

Electron Microscopy. Electron micrographs were obtained with an electron microscope (Hitachi Electric Industrial Co., Hitachi H-700).

RESULTS AND DISCUSSION

Methyl methacrylate was grafted onto the surface of carbon black by radical polymerization using AIBN as an initiator.⁷⁻⁸ It has been reported, however, that the degree of grafted polymer on carbon black in radical polymerization is low¹⁶ and that dispersions of GC in acetone were comparatively unstable.⁸ Ohkita et al.^{13,14} have found that the GC obtained by anionic polymerization with *n*-BuLi as an initiator gave a higher grafting ratio and exhibited a very stable dispersion in acetone. The reaction mechanism of the graft polymerization is explained as follows: MMA is graft-polymerized to active complexes formed by the reaction of the oxygen-containing groups present on the surface of carbon black with *n*-BuLi (see Fig. 1). Therefore, the longer time carbon black is pretreated with *n*-BuLi, the higher the amount of grafting becomes.

To clarify the electrical properties of GC obtained by the anionic polymerization, a variety of GC with different degrees of grafting were prepared under various reaction conditions. Anionic polymerization conditions of MMA in the presence of carbon black are shown in Table I. All anionic polymerizations were carried out at 0°C. M_1 – M_4 were polymerized using carbon black pretreated for 60 min at 0°C with *n*-BuLi, while M_5 – M_9 were polymerized by mixing monomer, initiator, and carbon black simultaneously. A large amount of methyl alcohol was then added to the reaction products and carbon black–polymer mixture was precipitated. This precipitate was dried in vacuum and the conversion was determined. The grafting ratio was obtained by Soxhlet extraction. The conversion increased with reaction time, and particularly, for M_5 – M_9 , the conversion increased rapidly in a short time. But the grafting ratio of M_5 – M_9 was small.

TABLE I
 Anionic Polymerizations of MMA in the Presence of Carbon Black

Sample designation	Carbon black Philblack O (g)	Monomer MMA (g)	<i>n</i> -BuLi (mL)	Solvent toluene (ml)	Pre- treated time (min)	Reaction ^a time (min)	Con- version (%)	Graft ratio (%)
M ₁	0.6	1.5	1.0	25	60	10	33	13.4
M ₂	0.6	1.5	1.0	25	60	120	75	34.4
M ₃	0.6	1.5	1.0	25	60	600	95	48.0
M ₄	0.6	3.0	1.0	25	60	5	81	51.0
M ₅	1.8	3.6	2.0	65	0	0.25	19	—
M ₆	1.8	3.6	2.0	50	0	1	50	—
M ₇	1.8	3.6	2.0	50	0	1.5	58	2.5
M ₈	1.8	3.6	2.0	15	0	10	73	3.0
M ₉	1.0	3.0	2.0	15	0	30	67	2.8

^a Reaction temperature 0°C.

On the other hand, for M₁–M₄, the MMA monomer was grafted to a considerable degree with an increase of conversion. Thus, the carbon black treated with MMA gave a stable colloidal dispersion. The resistors were made by coating the stable colloidal solution on a porcelain plate and drying in vacuum at 60°C for 8 h. Preparation conditions of the resistors are shown in Table II. The samples (R₁–R₉) were made using the GC prepared with the conditions of Table I. For a comparison with the resistors, R₁₀ and R₁₁ were prepared by radical polymerization and mixing methods, respectively. In Table II, the carbon black content of the resistors (R₁–R₁₀) was determined by the following equation.

$$\text{wt \% carbon black} = \frac{\text{wt carbon black used} \times 100}{\text{wt carbon black used} + \text{wt monomer converted to polymer}}$$

 TABLE II
 Preparation Conditions for Resistors

Sample designation	Preparation method	GC used	Content of carbon black (wt %)	Molecular ^a weight	Graft ratio (%)	Resistivity at 40°C (Ω-cm)
R ₁	Anionic	M ₁	54.8	—	13.4	1.3 × 10
R ₂	Anionic	M ₂	34.8	—	34.4	1.9 × 10 ³
R ₃	Anionic	M ₃	29.2	100,000	48.0	7.3 × 10 ⁴
R ₄	Anionic	M ₄	19.8	200,000	51.0	6.0 × 10 ⁷
R ₅	Anionic	M ₅	72.5	—	—	0.9
R ₆	Anionic	M ₆	50.0	—	—	1.9
R ₇	Anionic	M ₇	46.3	—	2.5	2.0
R ₈	Anionic	M ₈	40.7	190,000	3.0	7.6
R ₉	Anionic	M ₉	33.3	260,000	2.8	7.7 × 10 ²
R ₁₀	Radical ^b	—	35.0	20,000	—	3.2 × 10 ²
R ₁₁	Mixing ^c	—	33.3	—	—	2.9

^a Measured by the viscosity method.

^b Polymerization was carried out under the following conditions: MMA, 3.0 g; carbon black, 1.5 g; toluene as a solvent, 9 mL; AIBN as an initiator, 60 mg; reaction temperature, 95°C; reaction time, 8 h; conversion following polymerization, 92.8%.

^c The polymer used was prepared by anionic polymerization.

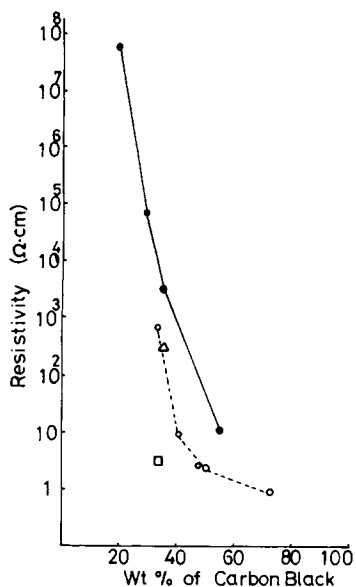


Fig. 2. Relationship between volume resistivity and wt % of carbon black. (●) R₁-R₄; (○) R₅-R₉; (Δ) R₁₀; (□) R₁₁.

The molecular weight of polymer in the resistors was estimated from that of the homopolymer separated from the carbon black-polymer mixture, as mentioned under resistivity. The molecular weight of the samples made by anionic polymerization was in the range of 100,000-260,000, while that of samples by radical polymerization was 20,000. It was reported that molecular weight of polymer obtained by radical polymerization of *n*-butyl acrylate in the presence of carbon black is about 8,000-10,000.¹⁷ The molecular weight of R₁₀ seems a little greater than the value of *n*-butyl acrylate, but smaller than that of samples by the anionic method.

The grafting ratio was higher in a series of R₁-R₄. However, these samples contained much homopolymer unattached to the carbon black, since the vinyl monomer itself polymerized. In a series of R₅-R₉, most of the polymer contained in the resistors was unattached to the carbon black: that is, the grafting ratio was smaller than 3%. Nevertheless, the dispersibility in toluene of the reaction products (M₅-M₉) was very good. It appears that the dispersibility in an appropriate solvent is improved¹⁶ by grafting only a small amount of polymer onto the surface of the carbon black. But the grafting ratio of R₁₀ could not be measured accurately, and the dispersibility of R₉ and R₁₀ was compared. As a result, that of R₁₀ was less than that of R₉.

The resistivities of the resistors obtained are shown in Table II. Apparently, a series of R₁-R₄ with a higher degree of grafting gave larger resistivities than a series of R₅-R₉. On comparison of R₂, R₁₀, and R₁₁ containing similar quantities of carbon black, the resistivity of the most grafted sample (R₂) was the largest, while that of sample (R₁₁) prepared by the mixing method was the smallest: i.e., R₂, $1.9 \times 10^3 \Omega\text{-cm}$ and R₁₁, $2.9 \Omega\text{-cm}$. That of the former was 10^3 times as much as that of the latter. The resistivity of R₁₀ prepared by the radical method was found between R₂ and R₁₁. From these results, it seems that the

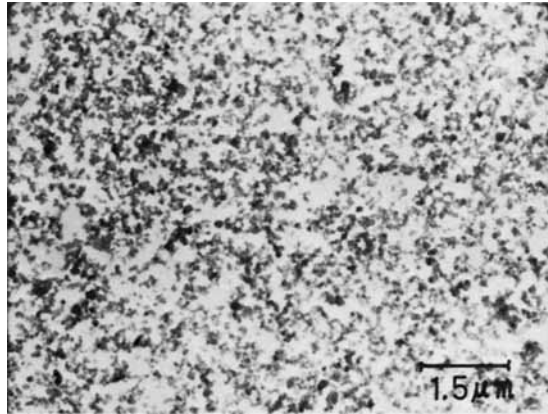


Fig. 3. Electron micrograph of GC obtained by an anionic polymerization. The sample (M_2 ; content of carbon black, 34.8 wt. %) was cut into slices of ca. 500 Å, fixed with osmium oxide and observed with an electron microscope, Hitachi H-700 (15,000 ×).

resistivities increased with an increase in grafting ratio. The phenomenon was briefly reported¹⁸ before and may be attributable to two effects. One effect is that carbon black disperses more uniformly into a polymer matrix, and then conductive paths formed through carbon black decrease. The other effect is that the surface of carbon black is wrapped separately by the graft polymer chain, resulting in isolation of polymer particles in the polymer. But it is difficult to consider these two effects separately, since carbon black wrapped by graft polymer disperses more uniformly. At any rate, the increase of the resistivity seems to be caused by isolation of the carbon black in the composition. An electron micrograph of the sample prepared according to M_2 is shown in Figure 3. It was found that aggregates composed of particles of several hundred Å were dispersed uniformly. Therefore, the flow of current is naturally restricted, as long as those particles are uniformly dispersed.

The resistance characteristics as a function of temperature (40–140°C) are shown in Figures 4–7. For resistors of low resistivity, resistance variation is

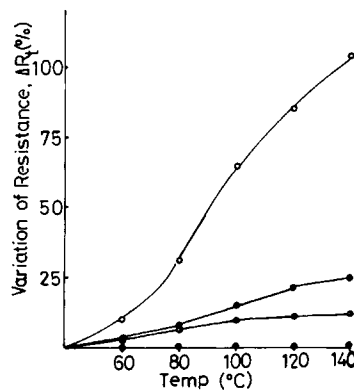


Fig. 4. Resistance variation–temperature curves of composite resistors obtained by anionic polymerization: (●) R_5 ; (○) R_6 ; (○) R_7 ; (○) R_8 .

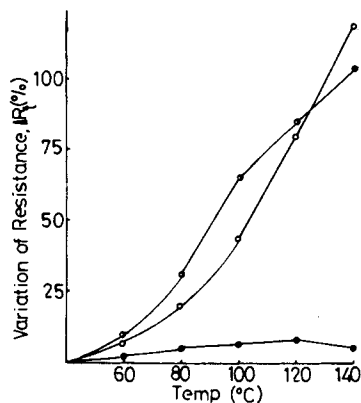


Fig. 5. Resistance variation-temperature curves of composite resistors obtained by various methods: (●) R_1 ; (●) R_8 ; (○) R_{11} .

presented by ΔR_t . Comparing the resistance variation with temperature for four resistors (R_5 – R_8) in the range of ca. 1–8 Ω -cm (see Fig. 4), the resistance variation was found to increase with a decrease in carbon black content, though the decrease of carbon black content gradually caused the resistivity (see Table II) to increase. In particular, the resistor (R_5) containing 72.5% of carbon black showed no anomaly with temperature change. Also, determination of the effect of grafting ratio was made. A comparison of R_1 , R_8 , and R_{11} with similar resistivities is shown in Figure 5. The grafting ratio of R_1 was the highest of the three, and R_{11} by the mixing method contained no polymer attached to carbon black. The resistance variation in R_1 , R_8 , and R_{11} (ΔR_{140}) was ca. 10%, 100%, and 120% respectively. It is interesting that R_1 with the higher grafting ratio and containing the most carbon black showed a smaller variation with rise in the temperature than the other two samples, though the resistivity of R_1 was only somewhat larger. As already stated, the contents of carbon black of these samples were different, though the resistivities were similar. It is likely,

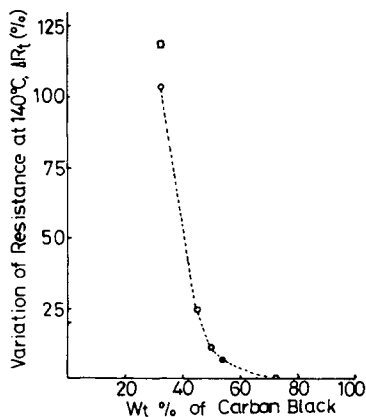


Fig. 6. Relationship between resistance variation at 140°C and wt % of carbon black for resistors with comparably smaller resistivity: (●) R_1 ; (○) R_5 – R_8 ; (□) R_{11} .

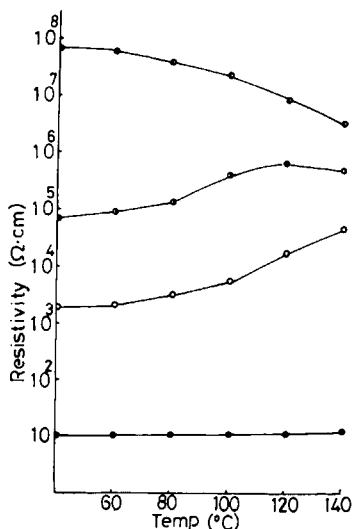


Fig. 7. Relationship between resistivity and temperature for resistors obtained by anionic polymerization: (●) R₁; (○) R₂; (●) R₃; (○) R₄.

therefore, that the resistance variation was affected by the content of carbon black. The resistance variation at 140°C, ΔR_{140} is plotted against wt % of carbon black in Figure 6. It was estimated from this figure that the resistance variation depended essentially on the content of carbon black. Narkis et al.¹⁹ have also pointed out that resistance variation against temperature increases with a decrease of carbon black in the range over a critical volume of carbon black, where resistance variation is maximum. Previously, the authors¹² reported that,¹² when 50 wt % of PMMA was mixed with 50 wt % of carbon black, the composition exhibited no glass transition temperature (T_g) in the range of 40–140°C and that the dilation of the polymer component in the composition was restricted by carbon black. Therefore, it is considered that, in the case of the GC containing more than 50% of carbon black, the dilation of the polymer component may be also restricted by the carbon black. This fact is pertinent to the application of carbon black-polymer composition to a variety of electrical devices. The GC obtained by anionic polymerization seems suitable for making a resistor device stable against temperature variation. This suggests that the resistor should be made so as to contain much carbon black, as long as a suitable resistivity is obtained. In contrast, it is better to increase the polymer content, when the desired resistivity is possible in designing a self-limiting temperature controlling heater using a large positive coefficient of resistance generally observed in such a composition material. The material prepared from anionic polymerization in the presence of carbon black seems suitable in the case of the former.

The resistivity-temperature relation of resistor (R₁–R₄) with high resistivity obtained by the anionic polymerization method is shown in Figure 7. For a resistor containing 34.8% carbon black, the resistivity was $1.9 \times 10^3 \Omega\text{-cm}$ at 40°C and, for that containing 29.2% carbon black, $7.3 \times 10^4 \Omega\text{-cm}$. These resistors showed a remarkably large positive anomaly, appearing in the range of 80–100°C corresponding to the T_g of PMMA. But R₃ showed no PTC characteristic above 120°C, where the resistivity was about $10^6 \Omega\text{-cm}$. Moreover, for R₄ with a lesser content of carbon black (19.8%), the resistivity was $10^7 \Omega\text{-cm}$ at 40°C, and the

temperature coefficient of the resistivity was negative. Nicodemo et al.²⁰ have reported that the resistivity of compositions with a high content of polymer decreases with raising temperature for polymer-metal composition system. It has been clarified that the conductive mechanism of a resistor with higher resistivity is different from that of resistors with comparably low resistivity. Probably, in resistors with high resistivity, the main electrical current can flow through the polymer layers in the carbon black, while, for resistors with low resistivity, the electrical current flows through a network consisting of carbon black aggregates.

CONCLUSIONS

The resistivity of the most grafted sample was the largest, while that of the sample without grafting was the smallest. It seems that the resistivity increases with an increase in grafting ratio. From a comparison of samples with similar resistivities, it was found that the stability of the resistor against temperature increases with an increase of grafting. Resistors of low resistivity prepared by anionic polymerization were very stable against temperature. The resistors with resistivities in the range of ca. 10^3 – 10^6 Ω -cm showed a remarkably large positive anomaly, but for a resistivity larger than 10^7 Ω -cm, the temperature coefficient was negative.

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