The Conduction Mechanism of Polymer–Filler Particles

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Synopsis

In this paper, the electrical properties and the conductive mechanism of polymer-filler particles are discussed using polymer-grafted carbon black. Resistors with resistivities in the range of ca. 10-10^8 Ω cm were made, and the resistance–temperature relationship was measured between 77 and 298° K. In this temperature range, the resistance decreased with an increase of temperature, suggesting that the electrical conduction is thermally activated. The resistance as a function of field strength was measured by a pulse method. The resistor was a resistivity of ca. 10^4 Ω cm showed field dependence, and the change of resistance was reversible. It was found that the resistance was independent of temperature at high field strength, and tunneling conduction is predominant. On the basis of these facts, theoretical equations were derived and compared with the experimental values.

INTRODUCTION

The electrical conduction mechanism in polymer–filler particle compositions has been discussed by many researchers.[1] It has been demonstrated that the electrical current flows through a network formed by conductive filler particles,[2–4] and that the electrical conduction through the network is controlled mainly by the gaps between the neighboring filler particles. Some authors[5,6] have suggested that the conduction is due to thermally activated electron hopping. Others[4,7,8] assumed that the electrons may tunnel through the thin polymeric films, if the polymer layer of the gap is extremely thin, i.e., less than 100 Å. However, the conduction mechanism is still not fully clarified.

The authors[9–11] have studied polymer-grafted carbon black (GC) to develop a resistors and a plane heater. GC materials are also useful to study the electrical conduction mechanism of polymer–filler particle compositions, because they are not only uniform, but also stable under various conditions, especially at high voltage.[12]

In this paper, a GC material made by grafting methyl methacrylate and glycidyl methacrylate to carbon black was used to investigate the conduction mechanism of the conductive compositions.

EXPERIMENTAL

Materials and Reagents

The carbon black was philblack O (HAF, N330) from Phillips Chemical Co. obtained through A. A. Chemicals Co. This carbon black contained 1.33%

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of oxygen. The specific surface area and the average diameter were 79.6 m^2/g and 29.4 nm, respectively.[13,14] 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. Monomers and cyclohexanone were obtained from Wako Pure Chemical Ind., Ltd., and purified according to the procedure of carbon black.

Polymerizations in the Presence of Carbon Black

The radical polymerizations of methyl methacrylate (MMA) and glycidyl methacrylate (GMA) in the presence of carbon black were carried out according to the procedure described[12] previously. Preparation conditions are shown in Table I.

Preparation of Resistors

Resistors were prepared according to the procedure described previously. Ethylene diamine, a curing agent, was added to the GC solution obtained. Then, the resistors were made by coating the dispersed paste on 18 mm wide rectangular porcelain plates with two electrodes separated by 18 mm, and by curing at a given temperature for 10 h after pre-curing. Preparation conditions are shown in Table II.

The Measurement of the Resistivity

The resistivity of the resistors was measured in a constant temperature chamber with a digital multimeter (Takeda Riken Industrial Co., Ltd., TR-6853).

The Measurement of the Resistance Change with Changes in Field Strength

The resistance change with changes in field strength was measured according to the procedure described[12] previously. A given voltage was applied to the resistors in a pulse of 15 ms, and the electrical current was measured.

TABLE I
Preparation Conditions of GC Materials[a]

Sample designation	Monomers		Carbon black[d] philblack O used (g)	Conversion (%)
	MMA[b] used (g)	GMA[c] used (g)		
G_1	7.01	1.99	3.0	94.8
G_2	4.69	1.33	3.0	98.1

[a] Polymerizations were carried out in 15 mL cyclohexanone for 8 h at 95°C with 0.03 g of azobisisobutyronitrile (AIBN) as an initiator and subsequently with additional 0.03 g of AIBN after 3 and 4 h, respectively.

[b] Methyl methacrylate.

[c] Glycidyl methacrylate.

[d] Treated with benzoyl peroxide.[12]

TABLE II
Preparation Conditions of GC Resistors

Sample designation	GC used	Ethylene diamine (g)	Cured conditions[a]		Carbon black (%)	Resistivity (Ω cm)
			Cured time (h)	Cured temp (°C)		
R_1	G_1	1.68	—	—	25	2.2×10^8
R_2	G_1	1.68	10	150	25	2.6×10^4
R_3	G_2	1.12	10	150	33	3.4×10
R_3'	G_1	1.68	10	200	25	2.6×10

[a] Samples were precured for 10 h at 100°C.

The Measurement of the Resistance Change with Frequency

The resistance change with frequency was measured with a LCZ meter (Yokogawa Hewlett Packard 4277A).

RESULTS AND DISCUSSIONS

Electrical properties of polymer–filler compositions are mainly characterized by the formation of a conduction network by contact conditions between neighboring filler particles in the network. In this paper, carbon black grafted with MMA and GMA was used as a conductive composition material. The resistors were made by curing the GC on a porcelain plate.

Preparation conditions of GC resistors and their resistivities are shown in Table II. The resistivity of a polymer–carbon black composition depends on the carbon black content, the dispersibility into a polymer matrix, and crosslinking conditions. In particular, the dispersibility of carbon black influences the conduction mechanism as well as the resistivity.[10,12] The dispersibility of carbon black in the GC was observed with electron microscopy and is shown in Figure 1. From these results, it was demonstrated that the resistivity decreases with the flocculation of carbon black, which accelerates the formation of the conductive paths. It should be noticed that for the resistor with ca. 26 Ω cm (R_3'), the network structure of carbon black is more developed than in the other two samples (R_1, R_2) in Figure 1. Consequently, the separation between carbon black properties in R_3 may have become less. On the basis, two conductive paths are pictured in Figure 2 which correspond to the main conductive paths of the resistors R_3 or R_3' in Figure 2(a), and that of R_2 in Figure 2(b), respectively.

The electrical field dependence of the resistance with the two resistors, R_2 and R_3, were measured and are shown in Figure 3. During the measurement, a voltage with a pulse of 15 ms was applied to reduce the influence of Joule heat. The resistance of R_3 was almost independent of the field (Ohmic behavior), at field strengths less than 300 V/cm, while that of R_2 decreased with an increase of field strength, especially at field strengths larger than 100 V/cm. The resistance change of R_2 was reversible, and the resistance of R_2 at a low field before and after measurement was nearly equal. Hence, the resistance change is not due to an irreversible change such as the rearrangement of the carbon black. Apparently, the difference between R_2 and R_3 at a high electrical field can be attributed to the con-

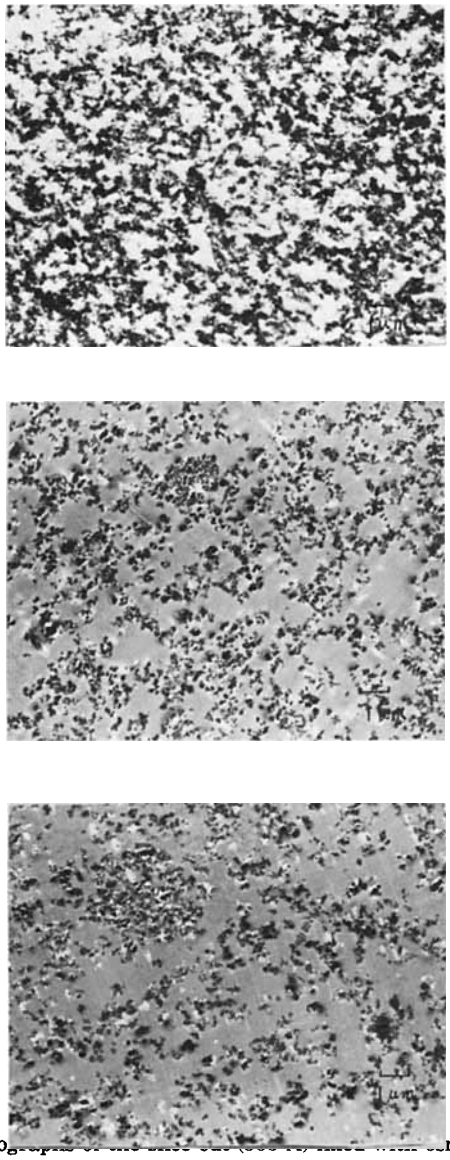

Fig. 1. Electron micro[illegible]mium oxide for the GC resistors.

duction mechanism. It is considered that for R_2, which contains more regions like that shown in Figure 2(b), a greater proportion of the electrical current can flow through thin polymer films by a tunneling mechanism at a high electrical field. On the other hand, the electrical current in R_3 is predominantly due to the thermal hopping of electrons through the contact regions between the neighboring carbon black particles.

The theoretical current due to thermally activated carriers is shown[15] in eq. (1) or (2):

$$i_1(T) = K_1 V \exp(-E_g/kT)^{1/n+1} \quad (1)$$

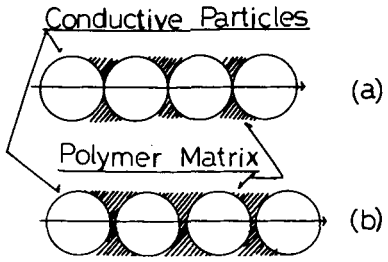

Fig. 2. Arrangement of carbon black in polymer matrix.

or

$$R_1(T) = (1/K_1)\exp(E_g/kT)^{1/n+1} \tag{2}$$

where $i_1(T)$ is the electrical current by the activated carriers thermally, $R_1(T)$ is the resistance, V is the applied voltage, E_g is the activation energy, k is Boltzmann's constant, and K_1 and n are constants.

The resistance–temperature relationship of R_2 in the range of -196 + 30°C was measured and applied to eq. (2). From the regression analysis, n was found to be approximately 3. The resistance was plotted against $T^{1/4}$ (see Fig. 4), and found to be linear against $T^{1/4}$. Then, E_g was obtained from the slope of the straight line in Figure 4 and has the value 0.35 eV.

By substituting the resistance, 43.2 MΩ at 293 K for eq. (2), K_1 becomes 8.2×10^{-6}. Then, eq. (2) can be expressed as following:

$$i_1(T) = 8.2 \times 10^{-6} V \exp[-8.0/T^{1/4})] \tag{3}$$

Tunneling current at a high voltage is expressed[16] in

$$i_2(T) = K_2 V^2 \exp[-8\pi(2m)^{1/2}(e\phi)^{3/2}d_g/3heV_g] \tag{4}$$

where $i_2(T)$ is the tunneling current at T°C, V_g is the gap voltage, g_g is the distance between the average gaps, ϕ is the height of barrier, m is the mass

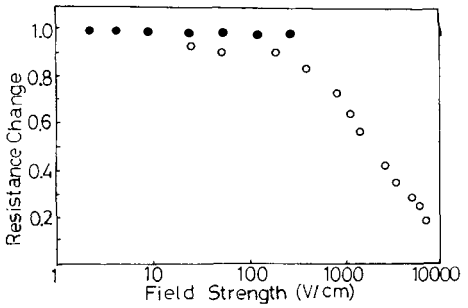

Fig. 3. Field dependence of resistance of GC resistors. (○) R_2; (●) R_3. Measured temp. 298 K.

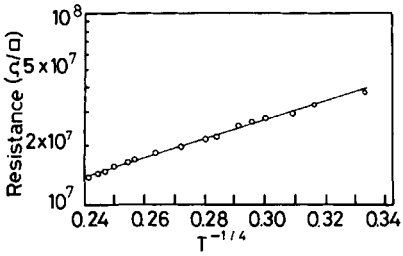

Fig. 4. Current–$1/T^{\frac{1}{4}}$ relationship of the GC resistor; sample, R_2.

of carrier, e is the magnitude of the charge on the electron, h is Plank's constant, and k_2 is a constant.

Equation (4) suggests that the tunneling current is independent of temperature and is proportional to the square of the voltage. The relationships between the electrcal current and the temperature at a constant electrical field were measured and are shown in Figure 5. For low electrical fields, the electrical current increased with an increase of temperature, but for relatively high fields, in particular, more than 2000 V/cm, the electrical current was constant regardless of the temperature. This fact suggests that, for low electrical fields, the electrical current follows a thermally activated hopping mechanism as expressed in eq. (2) or (3) and, for high electrical fields, the tunneling mechanism expressed in eq. (4) predominates.

By substituting the numerical value of e, m, and h in eq. (4),

$$i_2 = K_2 V^2 \exp[-(10^{-9}\phi^{3/2}d_g)/V_g] \tag{5}$$

Here, it is assumed that carbon black particles disperses uniformly and d_g is estimated from the following equation described by Polly and Boonstra[4]:

$$L = (\pi/6)d_A^3\rho_c \times 100/[(d_A + d_g)^3 - (\pi/6)d_A^3\rho_r + (\pi/6)d_A^3\rho_c] \tag{6}$$

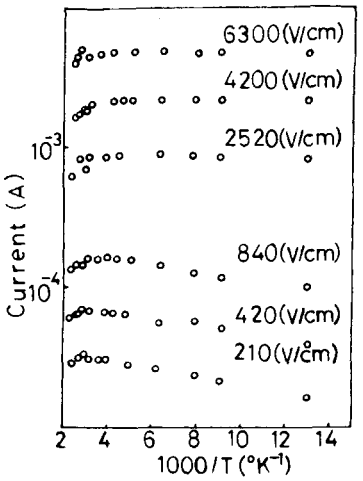

Fig. 5. Temperature dependence of electric current; sample, R_2.

where L is wt % of carbon black, ρ_r is the polymer density, and ρ_c is the carbon black density. For the sample R_2, L, ρ_r, ρ_c, and d_A are 25%, 1.2, 1.8, and 470 Å, respectively.

Thus, d_g becomes ca. 77 Å. Also, 2 is used for ϕ in accordance with Ohe and Naitoh's report.[7] Considering that $V_g \simeq 3.0 \times 10^{-5}$ can be roughly calculated from $V_g = V/N \simeq 3.3 \times 10^4 V$, the exponential component in eq. (5) becomes approximately 1 (N is the gap number calculated from the carbon black content).

As a result, for high electric fields,

$$i_2(T) \simeq K_2 V^2 \tag{7}$$

From (4) and (7) the total current i_t for relatively high electric fields is expressed in the following:

$$i_t = 8.2 \times 10^{-6} V \exp[-(8.0/T^{1/4})] + K_2 V^2 \tag{8}$$

For the sample R_2, K_2 is 6.7×10^{-9} using $i_t = 6.52$ mA and $V = 900$ V at 293 K:

$$i_t = 8.2 \times 10^{-6} V \exp[-(8.0/T^{1/4})] + 6.7 \times 10^{-9} V^2 \tag{9}$$

Using eq. (3), (9), experimental result for R_2 at 293 K were compared with the theoretical one in Figure 6. Apparently, the experimental values are in line with the theoretical ones.

The frequency dependence of the GC resistor was observed.

Generally, an equivalent circuit for polymer–filler particles can be depicted as shown in Figure 7, where R_g is the resistance of the interparticle, R_c is the resistance of a filler network, and C_g is the capacitance of the interparticle. For the samples of R_2 and R_3, R_g is much greater than R_c, and, therefore, R_c can be neglected. The impedance of the circuit is expressed as the following:

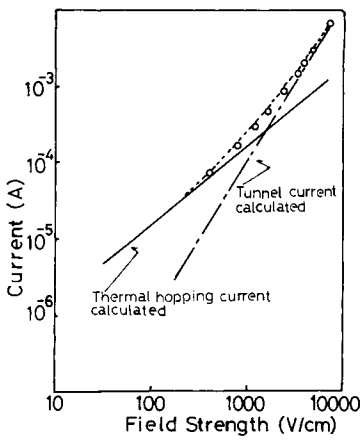

Fig. 6. Total current is plotted against field strength for R_2: (- - -) total current calculated; (○) total current measured.

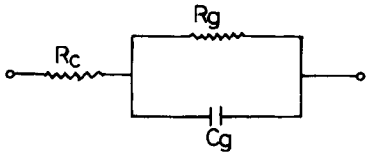

Fig. 7. Equivalent circuit of polymer–filler particles composition. R_g and C_g are the resistance and the capacitance between the neighboring particles, respectively. R_c is the resistance of a network consisting of the particles.

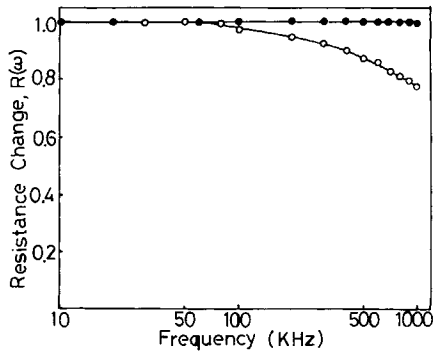

Fig. 8. Frequency dependence of resistance. (○) measured for R_2; (●) for measured R_3; solid lines show calculated values for R_2 and R_3, respectively.

$$Z_f = R_g/(1 + \omega^2 C_g^2 R_g^2) - j(C_g R_g^2 \omega)/(1 + C_g^2 \omega^2 R_g^2) \tag{10}$$

The real part of this expression is the effective ac resistance. The ratio of the ac resistance to the dc resistance, $R(\omega)$, is expressed in the following:

$$R(\omega) = 1/(1 + \omega^2 C_g^2 R_g^2) \tag{11}$$

The experimental values were compared with the theoretical ones in Figure 8. The measured values almost agreed with the calculated ones.

CONCLUSION

The electrical mechanism of polymer–filler particles was discussed using resistors made from GC materials. The electrical conduction is controlled mainly by two mechanisms. At low field strength, the conduction is due to thermally acitivated electron hopping, while, at high field strength, tunneling conduction is predominant. On the basis of the facts, the theoretical equations were derived.

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