Effect of Cohesive Property of Carbon Black on Electrical Conduction of CB–Resin Composites

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ABSTRACT: The temperature dependence of carbon black(CB)–resin composites has been studied in the wide temperature range from $-160°C$ to $220°C$ by changing the curing temperature. Resistance of the composite decreases at first and increases around $70°C$ and then irreversibly decreases above the glass transition temperature of binder resin for ascending temperature. The minimum and maximum of resistance on the temperature dependence have been discussed from the point of view of cohesive property of CB particle and physical property of resin.
     KEY WORDS   Carbon Black / Epoxy / Electrical Property / Compsoite / Resistor /

Many experimental efforts on carbon black(CB)–resin composites have been devoted over several decades to electrical studies of the basic phenomena. They have discussed the physical basis and mathematical formalism for the three important processes such as percolation, tunneling and thermal expansion which are controlling the electrical conduction.

Percolation theory predicts a sharp increase in the conductivity at a critical volume fraction of conductor, which is approximately 0.25 for a random dispersion of irregularly shaped particles.[1-3] However, the critical volume fraction for CB–resin composite strongly depends on the natures of binder resin and CB particle. For example, the higher polarity of a polymer gives a larger critical volume fraction because a large surface tension of polymer produces a large excess energy in the polymer–CB interface.[4] A highly structured carbon shows a small percolation threshold; even if the volume fraction of CB is less than 0.1, a sharp increase of conductivity has been observed.[5,6] Thus, CB–polymer composites are extremely complex in their percolative behavior

in contrast to metal-particle-filled systems.

Change of the electrical conduction with temperature are dominated by the intrinsic matrix conduction and tunneling conduction across the thin layers separating neighboring CB particles. A quantum mechanical tunneling conduction has been presented by Sheng[7] which is well applied to explain the temperature dependence of electrical conduction in CB–poly(vinyl chloride) composites at cryogenic temperatures below 100 K.

Generally, the electrical conduction of CB–resin composites shows a U shaped dependence on temperature.[8,9] The negative temperature coefficient (NTC) of resistance is ascribed to the tunneling conduction which is enhanced by thermally fluctuations.[7,10,11] Amorphous carbon films also show NTC of resistivity above liq. N_2 temperatures, which is explained by the thermally assisted hopping conduction mechanism.[12] A large positive temperature coefficient (PTC) of resistance is observed near the melting point of polymer, being due to widening the gap between CB particles or decreasing of CB content by

thermal expanison of resin.[8,13-16] By heating the composite above melting point, the resistivity shows a mild decrease or sometimes a mild increase with acending temperature.[15,16] The change of resistivity above melting points has not been discussed in detail. However, the sudden transition from PTC to NTC strongly depends on particle size, aggregate shape or structure, and porosity of CB.[15,16]

It is well known that the CB–resin resistor has an advantage due to its cheap manufacturing cost. However, there are also disadvantages such as a large temperature coefficient of resistance (TCR) and a large humidity coefficient of resistance (HCR).[17] In order to improve the TCR and HCR of CB–polymer resistor, we have studied, at first, the mechanism of the electrical conduction of the composite by changing the properties of polymer and CB.[9] By incorporating the effect of thermal expansion of resin into the CB gap, the temperature dependence of resistance of CB–polymer composites from liq. N_2 temperature to 150°C has been tried to explain using the thermally activated tunneling process.[7] The modified tunneling process showed a change from NTC to PTC of resistance. However, the calculated results using the model could not explain the temperature dependence of the resistance on the CB content.[9] Therefore, we have presented a model, which is based on a deliberately modified conduction mechanism based upon Scarisbric's model[18] by incorporating thermal expanison of resin and thermally activated electrical conduction process. The conducting paths formed by CB particles was assumed to be a thermally activated process in the electrical conduction. And, the thermal expansion of resin was assumed to cause the conducting paths to break off or the gaps between CB particles to enlarge. This effect of thermal expansion of resin on the electrical conduction has been experimentally confirmed by changing the thermal expansion of resin.[19] As a result of these competitive processes, the temperature dependence of the resistance shows a U shaped curve for temperature. The model can explain a U-shaped dependence of resistance using reasonable parameters such as the activation energy of resistance in low temperatures, the thermal expansion coefficient of polymer, and the value of volume fraction of CB.

The cohesive property of CB particles is practically very important because the change of resistance by humidity is caused by enlarging the gaps due to swelling of the binder resin. This is the same mechanism to the temperature dependence of resistance, where the thermal expansion of resin is effective.[19,20] Therefore, it is important how the cohesive property of CB can be changed by curing temperature.

In this paper, we shall exmaine the model from the point of view of a cohesive property of CB and a physical property of resin. The temperature, where the minimum of resistance appears, comes from a result of a competitive process between the NTC and PTC processes. Therefore, the temperature is a measure of the cohesive property of CB particles. It is one of the aim of this paper to clarify how the temperature giving the minimum resistance is changed by properties of CB or epoxy resin and by curing temperature.

The other aim of this paper is to describe the behavior of electrical conduction of the composite around the glass transition temperature of epoxy resin.

EXPERIMENTAL

In the experiments, six furnace CB's from low structure to high structure are used, and the physical and chemical properties of them are shown in Table I. They are listed from left side to right side in the order of from large surface area to small surface area. The CB1 is Black Pearls 2000 (Cabot Co., Ltd.), CB2 Ketjenblack EC (Japan EC Co., Ltd.), CB3 Vulcan XC-72 (Cabot Co., Ltd.), CB4 and CB5 MA600 and MA100, respectively, (Mitsubishi Petrochem. Co., Ltd.), and CB6 HS-500 (Asahi

Table I. Physical and chemical properties of used carbon blacks

	CB1	CB2	CB3	CB4	CB5	CB6
Surface are/ $m^2 g^{-1}$	1475	950	257	153	134	37
Oil absorption/ /ml/100 g	330	350	265	124	101	447
Particle size/ nm	15	30	18	18	22	76

Table II. Chemical properties of epoxy resins and blending ratio

	WPE (g/eq)	Hardener	Accelerator
E825	175	85 phr	1 phr
E828	186	80 phr	1 phr

Carbon Co., Ltd.) The physical and chemical properties of CB vary with particle size, porosity, and the oxygenated structures combined with their surface. Usually, a high structure CB, which has a large value of surface area or a large value of oil absorption, easily makes a good aggregation form for electrical conduction.[21] The resins used were two kinds of glycidyl ether epoxy (E828 and E825, Yuka Shell Epoxy Co., Ltd.). The hardener used was acid anhydride (DX126, Yuka Shell Epoxy Co., Ltd.). The accelerator used was imidazole derivative (EMI24, Yuka Shell Epoxy Co., Ltd.). The blending ratio of them and chemical properties of resins are listed in Table II. The volume fraction of CB, f_v, which is the volume ratio of CB to the sum of volumes of CB and resin, and the experimental conditions such as curing temperature, T_c, curing period are shown in each figure.

After mixing epoxy resin with CB for 1 h *in vacuo*, it was printed on a ceramic substrate using the screen method. The pattern is shown in Figure 1. After the pattern had been pre-cured for 2 h at 100°C, it was cured mainly for 20 h at 165°C or 220°C in air.

Temperature dependence of the CB–resin composite was measured by heating at
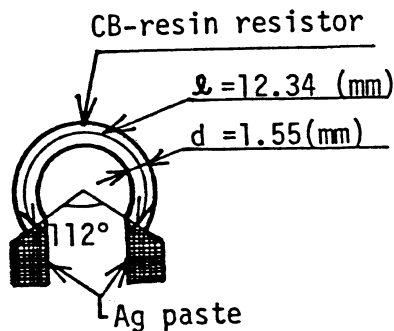
Figure 1. Printed pattern of the CB–resin composite by the screen method.
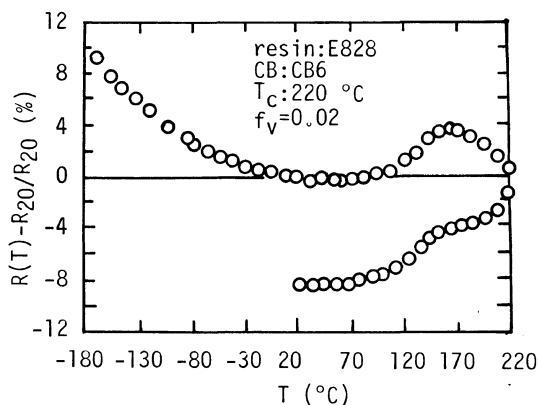
Figure 2. Typical temperature dependence of the resistance of CB–resin composite. (Resistivity, ρ, of each resistor is about $10^2 \,\Omega\,cm$.)

1°C min⁻¹ from about -160°C to 220°C *in vacuo*. The change of resistance is expressed as a percent change of resistance for the resistance, R_{20}, at 20°C; the resistance, R_{20}, is used as a reference.

RESULTS

Figure 2 shows a typical temperature dependence of the CB–resin composite. It can be seen from -160°C to 220°C that the resistance once decreases and then starts to increase around 70°C and finally decreases again for ascending temperature. At 220°C, the temperature was held for 10 min. After that, the composite was cooled down without
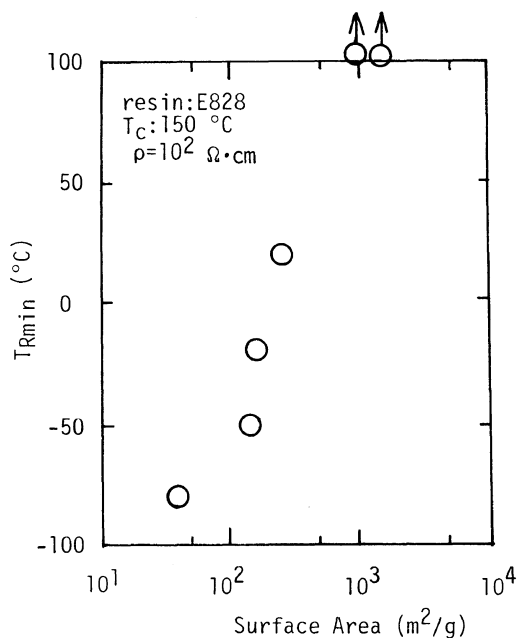
Figure 3. $T_{R\,min}$ as a function of surface area, SA, of CB. (Each volume fraction of the composite varies from sample to sample, but the resistivities for them are constant at $10^2\,\Omega\,cm$.)

electrical power. Then, the resistance was irreversibly decreased. When heating was below about 140°C, the temperature dependence of the resistance traced the same path for heating and cooling cycles. As there are a minimum of resistance around 45°C and a maximum around 165°C on heating cycle, we shall discuss the temperatures $T_{R\,min}$ and $T_{R\,max}$, at which the resistance shows a minimum and maximum, respectively.

Experimental Results in Low Temperature

From the point of view of the property of CB, the $T_{R\,min}$ strongly depends on the surface area, SA, of CB as shown in Figure 3, where each resistivity for the composites made of various CB's is almost about $10^2\,\Omega\,cm$. Because the $T_{R\,min}$'s for CB1 and CB2 are beyond 100°C, the data of them are indicated with arrows in the figure. It can be seen that the $T_{R\,min}$ of the composites made of CB of larger SA shifts to higher temperatures.
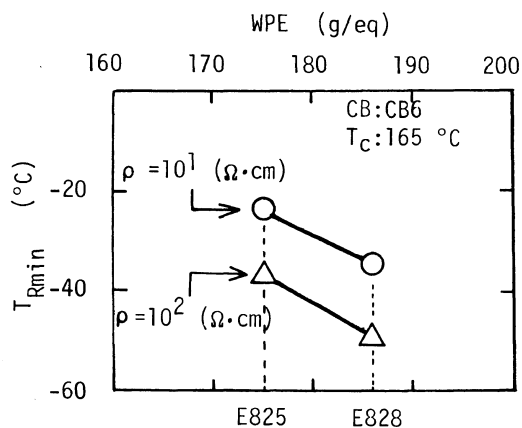
On the other hand, $T_{R\,min}$ also depends on

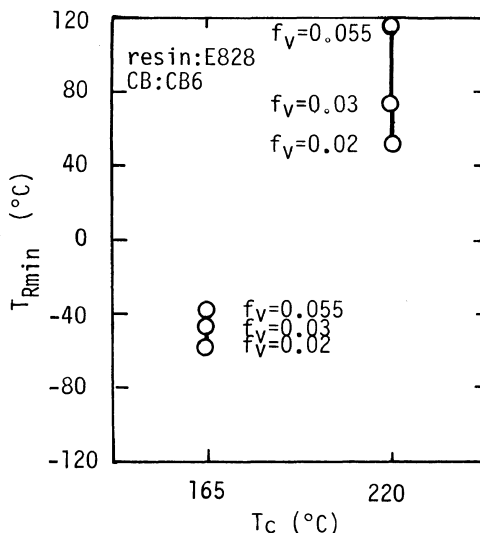**Figure 4.** $T_{R\,min}$ as a function of weight per epoxide (WPE).

Figure 5. Dependence of $T_{R\,min}$ on curing temperature T_c.

the weight per epoxide equivalent (WPE) of epoxy resin. Figure 4 shows the dependence of $T_{R\,min}$ on WPE. The value of $T_{R\,min}$ shifts to higher temperatures when the WPE becomes small. From the figure, it can be also seen that $T_{R\,min}$ moves to higher temperatures with decreasing resistivity by loading more CB content.

As shown in Figures 3 and 4, the $T_{R\,min}$ is influenced by the properties of CB and resins. It is also changed by curing temperature T_c. Figure 5 shows the dependence of $T_{R\,min}$ on T_c.
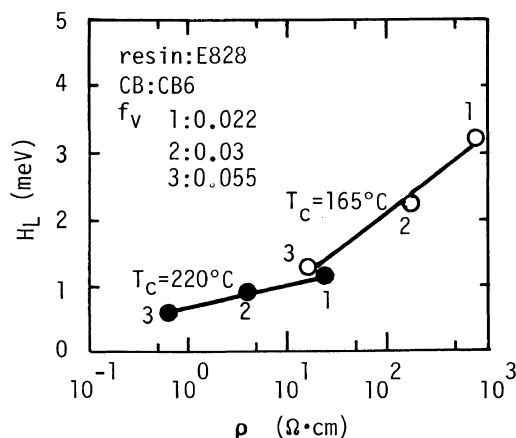
Figure 6. Dependence of the activation energy, H_L, of the resistance in the low temperature region below $-20°C$ on resistivity.

The CB and resin used were CB6 and E828, respectively. The change in $T_{R min}$ by T_c is extremely large and is as much as that by varying the property CB as seen in Figure 3.

Figure 6 shows the dependence of the activation energy H_L on resistivity obtained from Arrhenius' equation in the low temperature region below $-20°C$. The volume fractions of the composites cured at 220°C are the same as those at 165°C. Values of H_L for the composites cured at $T_c = 165°C$ are in the range from 1 meV to 3 meV and decrease with decreasing resistivity. Values of H_L were decreased by curing at high T_c of 220°C.

Experimental Results around Glass Transition Temperature

In Figure 7, $T_{R max}$ is shown as a function of f_v. The glass transition temperature, T_g, of E828 cured at $T_c = 165°C$ exists around 137°C as shown in Figure 7. By curing at 220°C, T_g shifts to lower temperature. This lowering may be due to a thermal degradation of resin caused by high T_c. It is important to clarify the change of $T_{R max}$ by curing temperature. Namely, the values of $T_{R max}$ are below T_g for curing temperature of 165°C. On the other hand, $T_{R max}$ shifts to much higher temperature than T_g by curing at 220°C nevertheless the T_g of
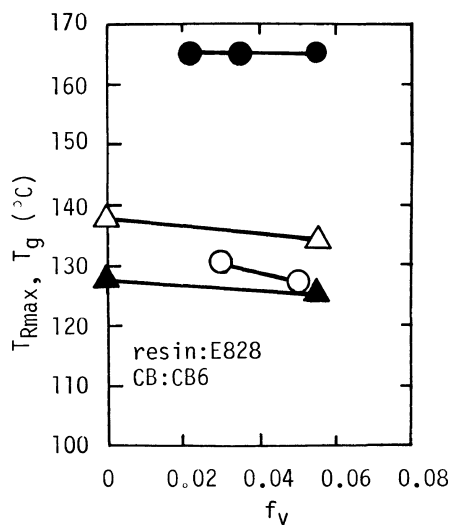
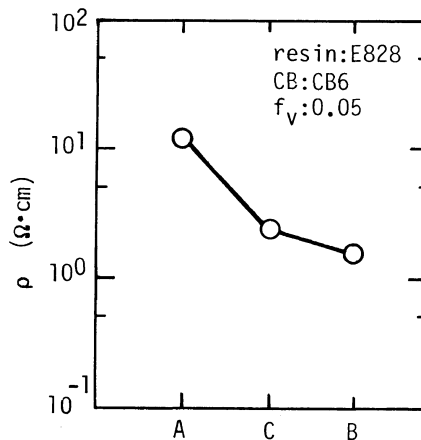**Figure 7.** T_g and $T_{R max}$ as a function of the volume fraction, f_v, of CB.

Figure 8. Change of resistivity by curing conditions. Condition A means that $T_c = 165°C$, B for $T_c = 210°C$. Condition C means that the conditions B was applied after condition A.

the resin cured at $T_c = 220°C$ shifts to a lower temperature than that at $T_c = 165°C$, which is at least by 30°C higher than that at $T_c = 165°C$.

Figure 8 shows the change in resistivity by

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curing conditions. The condition A on the abscissa indicates that T_c is 165°C, and the condition B is $T_c = 210$°C. The condition C means that the composite was cured again at 210°C after it had been previously cured at 165°C. The resistivity of about $2.5 \times 10^1 \, \Omega$ cm for $T_c = 165$°C (condition A) is almost by a factor of 10 larger than that for $T_c = 210$°C (condition B). The resistivity for condition C is decreased by the further curing and is close to the resistivity for the composite cured at 210°C as shown in Figure 8.

Humidity Dependence of Resistance

The humidity dependence of resistance was measured by changing the relative humidity of environment. The percent change of resistance was normalized by the resistance at 40% relative humidity. Usually, the percent change of resistance shows a linear dependence on the relative humidity.[22] Therefore, the value of humidity coefficient of resistance (HCR) was estimated from the slope on the relative humidity (%)–percent change of resistance (%) curve. The value of HCR means that how much the percent resistance changes by 1% relative humidity. Figure 9 shows the HCR as a function of f_v. The HCR strongly depends on f_v for $T_c = 165$°C. On the other hand, the magnitude of HCR for $T_c = 220$°C and the change of HCR with f_v are smaller than that for $T_c = 165$°C.

DISCUSSION

We have studied widely the temperature dependence of the resistance of the CB–resin composite in the range from about -160°C to 220°C in order to clarify how the cohesive property of CB particle changes by curing temperature, properties of CB, and resin. As shown in Figure 2, the resistivity decreases with raising temperature below room temperature. It has been concluded that the electrical conduction in low temperatures is governed by the thermally activated mechanism. However,
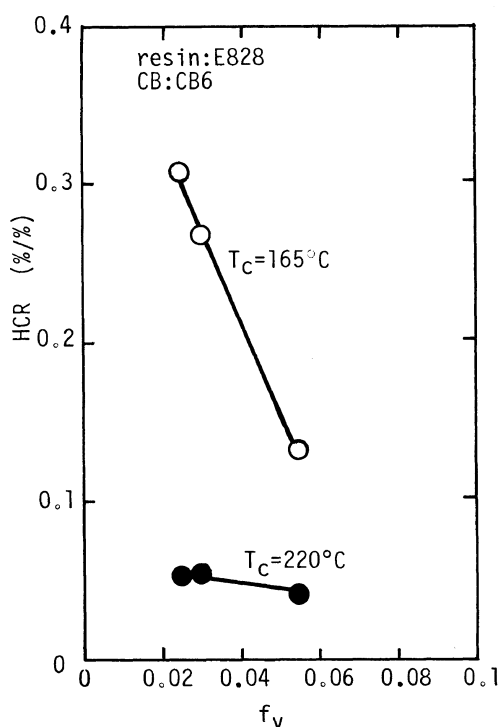

Figure 9. Dependence of HCR on carbon black content f_v.

once the thermal expansion of resin begins to be effective for breaking off the conducting paths or for enlarging the gap of CB particles, the resistance increases with raising temperature. As a result, $T_{R\,min}$, where the resistance shows a minimum, appears on the temperature dependence. Therefore, it is not unreasonable that $T_{R\,min}$ indicates a measure of cohesive property of CB particles. It is well known that the high structure CB's such as CB1 and CB2 show a high conductivity even if the f_v of them is far less than that of low structure CB.[5,6,9] That means that the high structure CB's tend to easily form conductive paths. From Fig. 3, the $T_{R\,min}$ shifts to higher temperatures with a larger value of SA. It is, therefore, conclusive that a high strucuture CB shows more strong cohesion than a low structure CB. The important thing in this paper is that this cohesion is drastically enhanced by curing at

high temperature as shown in Figure 5.

By curing for 20 h at above 165°C, a thermal degradation of epoxy resin may take place by causing oxidation and chain scission as suggested from a lowering of T_g. An epoxy resin cured at higher temperature shows larger water absorption, which is ascribed to the thermal degradation.[23] In Figure 9, HCR was decreased by curing at high temperature. There are two reasons for the decrement of HCR by adding CB; one of them is a decrement of resin and the other is due to forming a strong cohesive structure by adding CB. Previously, we have presented that the change of resistance with humidity is due to a swelling of resin.[19,20,22] Therefore, the decrement of HCR by curing at high temperature is due to a formation of strong cohesion of CB particles against swelling of resin.

The activation energy of the resistance in low temperatures as shown in Figure 6 decreases with decreasing resistance or by curing at high temperature. It means that the required thermal energy is decreased with shortening the gap between CB particles by loading CB or by curing at high temperature. It should be noticed that the thermal expansion of resin makes the activation energy small when it is effective in the low temperature region. The results shown in Figure 4, that the resin of smaller WPE gives a higher $T_{R\,min}$, seem very reasonable because the resin of smaller WPE tends to give a smaller coefficient of thermal expansion and a higher glass transition temperature.[20,22,24] Miyauchi *et al.* have presented the same result that an apperance of PTC is prevented by proceeding a crosslinking of resin.[25]

By heating to above $T_{R\,min}$, the resistivity decreases around $T_{R\,max}$. It can be concluded that the decrement in resistivity is caused by a re-cohesion of CB so as to increase a number of conducting paths or to shorten the gap of CB particles under the rubber state of resin. Micro-Brownian motion of resin may enhance the re-cohesion of CB particles, because the change of the resistivity is irreversible for cyclic

heating up to 220°C.

As seen from Figure 7, $T_{R\,max}$ moves to very high temperature by curing at high temperature though the glass transition temperature seems not to change as much as $T_{R\,max}$. It can be said that the shift of $T_{R\,max}$ on curing temperature is also another example indicating the cohesive property of CB particles.

CONCLUSIONS

Temperature dependence of CB–resin composites has been studied widely from $-160°C$ to 220°C. There are a minimum and a maximum of resistance on the temprature dependence.

The minimum of resistance appears as a result of competitive process between the decrement of resistance by thermally activated process and the increment of resistance by enlarging of the gaps of CB particles or by breaking off the conducting paths due to thermal expansion of resin. By heating above the glass transition temperature up to 220°C, the resistance irreversibly decreases. It is caused by a re-cohesion of CB particles under the rubber state of resin.

The $T_{R\,min}$, where the minimum of resistance appears, is a measure of cohesion property of CB particles. It shifts to higher temperatures by using a high structure CB and by curing at high temperature because of strong cohesion. Also, it shifts to higher temperatures by using a resin of smaller WPE because of small thermal expansion coefficient. The above experimental results support the electrical conduction model for the CB–resin composite which we have proposed before.[9,19]

The $T_{R\,max}$, where the resistance shows a maximum, also appears as a result of a competitive process between the enlargement of the gap of CB particles or the break off of the conducting paths and the re-cohesion of CB particles. It leads to a strong dependence of $T_{R\,max}$ on the cohesive property CB particle.

It has been presented that the humidity

dependence of CB–resin resistor can be improved by changing a curing temperature.

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