Electrical Conductivity of Carbon Fibers/ABS Resin Composites Mixed with Carbon Blacks

GUANGHONG LU,* XIAOTIAN LI, HANCHENG JIANG, and XIANGJUN MAO

Department of Materials Science, Jilin University, People's Republic of China

SYNOPSIS

In this article, the electrical conductivity of composites with different ratios of carbon fiber (CF) content to carbon black (CB) content was studied. The CF content is the main factor to determine the resistivity of the composites filled with CF and CB. The conduction mechanism for this kind of composite is discussed. From comparison of the resistivity of the composites filled with CF and CB with that of the composites filled with CF only, it is shown that using CB as a substitute for part of the CF in CF-filled composites can decrease the production cost, but hardly change the conductivity. The optimum substitution amount is 5% when CF content is beyond 10% in the composites. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Electromagnetic shielding polymer composites have been developing very rapidly in recent years, especially conductive polymeric composites filled with carbon fibers,[1-4] which have many advantages such as their good mechanical properties, significant reinforcing effect, and lightweightness, thus being suited to make "light-type" shielding materials, and are easily molded by extrusion or injection, thus being suited to be processed in batches, etc. These materials have a wide range of applications in military, industrial, and commercial aspects; e.g., they can be used in shells of computers and television sets to shield electromagnetic waves, and thus, allow them work safely.

However, an obvious weakness of the shielding materials filled with carbon fibers (CF) is that their production cost is very high due to the high price of CF. This weakness restricts the range of application for this kind of shielding material. In our work, to decrease the production cost, we use carbon blacks (CB) to substitute part of the CF in the composites because of the very low price of CB. Few authors, to our knowledge, have studied the conductivity of the composites filled with both CF and CB, especially the aspects of decreasing the production cost. In this article, emphasis was laid on the electrical conductivity of CF/ABS resin composites mixed with CB.

EXPERIMENTAL

Materials

The materials used in this work are acrylonitrile–butadiene–styrene (ABS) resin and PAN-based type T300 CF, whose density is 1.60 g/cm^3; diameter, 7 μm; and volume resistivity, 1.6×10^{-3} Ω cm, and CB, whose average size is 60–70 mm; specific surface area, 230 m^2/g; DBP value, 280 mL/100 g; and PH value, 7–9.

Mixing Method

1. Solvent method of mixing: First, ABS resin was put in chloroform to form a "paste"; then, CF, which was chopped into 5 mm lengths, and CB was dispersed into the paste by mechanical stirring according to the proportion. The paste after mixing was dried at room temperature.
2. Brabender mixing method: Both CF, which was chopped into 5 mm lengths, and CB were mixed with ABS resin by a Brabender operating at about 210°C for 4–5 min.

---

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 62, 2193–2199 (1996)
CCC 0021-8995/96/132193-07

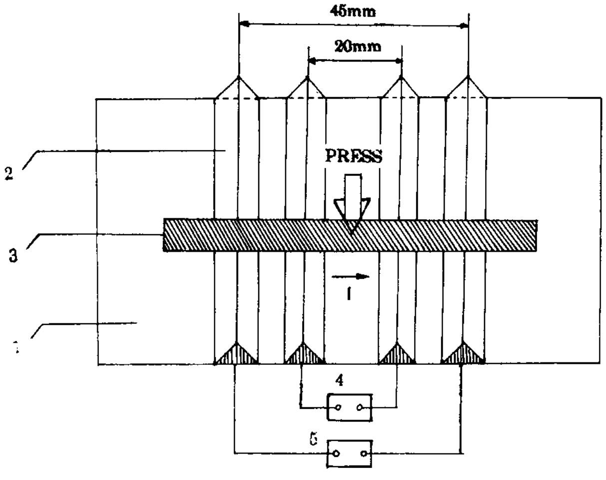

Figure 1 Illustration of the mechanism of resistance measurement by volt-ampere method. (Press direction is vertical to the plane of plastic plate.) (1) Insulating plastic plate; (2) copper electrode; (3) sample; (4) millivoltmeter; (5) milliammeter.

Sample Preparation

The composites after mixing using the methods above were molded by hot pressing at 200–210°C for about 5 min. Then, they were cut into stripes of size 60 × 3 × 2 mm. Four samples were prepared for the same composites.

Resistance Measurement

Resistance was measured by the Volt-ampere method. Figure 1 is an illustration of the mechanism of this method. The resistance of each of the four samples was measured and an average value was obtained. A Type 2575 eight digital millivoltmeter and Type 2553 dc voltage current standard made by YEW Co., U.S.A., were used. The contact resistance was eliminated by a double-lead-wire method.

Measurement of Fibers' Aspect Ratio

To determine the aspect ratio (*L*/*D*) of the fibers after mixing, the composites were put in chloroform. The resin phase was dissolved and the fibers remained. Then, the fibers were extracted and observed under an optical microscope. By measuring the length of 100 fibers and calculating the average value, the aspect ratio of the fibers can be obtained.

RESULTS AND DISCUSSION

Conductivity of CF/ABS Resin Composites Mixed with CB

The variation of the resistivity of the ABS resin mixed with CF and CB with filler content is indicated in Figures 2 and 3. Figure 2 shows the composites mixed by the solvent method, in which curves a and d represent the composites filled with CF and CB, respectively; curves b and c represent the composites filled with fillers which have a different mixing ratio of CF content to CB content—for curve b, CF content to CB content is 1 : 1, and for curve c, CF content to CB content is 1 : 2. Figure 3 shows the composites mixed by a Brabender, in which curves a and e represent the composites filled with CF and CB, respectively, and the CF content to CB content of curves b, c, and d is 3 : 1, 2 : 1, and 1 : 1, respectively. From these two figures, it is shown that whichever mixing method and whichever filler (CF, CB, or both CF and CB) were used, the resistivity of the composites decreases with increase of the fillers. For the same filler content, the greater CF proportion in the fillers, the lower is the resistivity of the composites, whichever mixing method was used. Two extreme cases are when only CF was filled but no CB (curve a in both figures)—the resistivity of the composites is the lowest in the group—and only CB was filled but no CF (curve d in Fig. 2, curve e

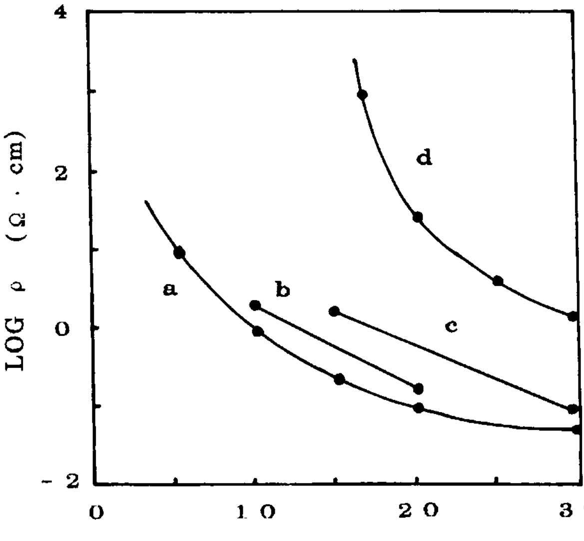

Figure 2 Variation of the resistivity of CF/ABS resin composites filled with CB mixed by the solvent method with filler content: (a) CF; (b) CF : CB = 1 : 1; (c) CF : CB = 1 : 2; (d) CB.

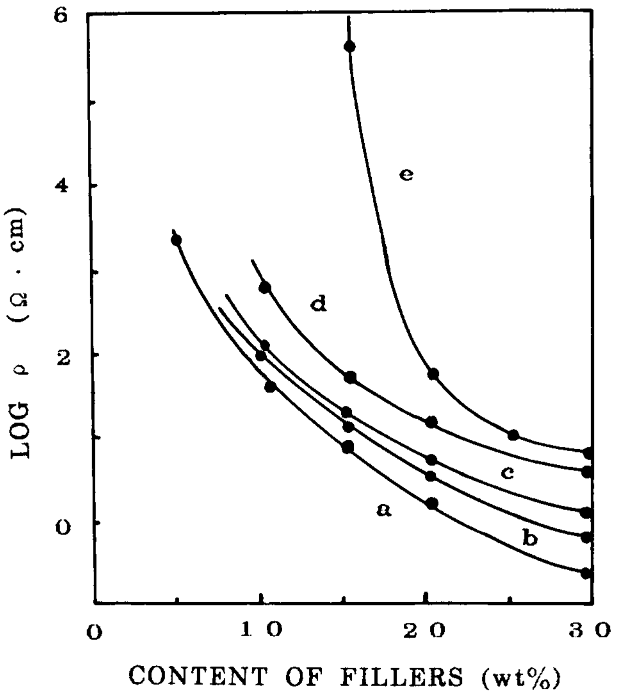

Figure 3 Variation of the resistivity of CF/ABS resin composites filled with CB mixed by a Brabender with filler content: (a) CF; (b) CF : CB = 3 : 1; (c) CF : CB = 2 : 1; (d) CF : CB = 1 : 1; (e) CB.

in Fig. 3)—the resistivity of the composites is the highest in the group. Curves that represent different mixing ratios of CF content to CB content are all between these two figures. From curve d in Figure 2 and curve e in Figure 3, if only CB is filled in the composites, it is difficult for the resistivity of the composites to be lower than 1 Ω cm.

Figure 4 is the variation of the resistivity of the composites mixed by the solvent method with CB content when CF content is fixed. The fixed CF content of curves a, b, and c are 0, 5, and 10%, respectively. Figure 5 is a variation of the resistivity of the composites mixed by a Brabender with CB content when CF content is fixed. The fixed CF content of curves a, b, and c are 0, 10, and 15%, respectively. These two figures show that if CF content is fixed, the resistivity of the composites decreases with the increase of CB content and varies slowly when the CB content is beyond 10% whichever mixing method is used.

Figures 6 and 7 show the relationship between the resistivity of the composites and CF content when CB content is fixed. Figure 6 illustrates the composites mixed by the solvent method; the fixed CB content of curves a, b, c, and d are 0, 5, 10, and 20%, respectively. Figure 7 illustrates the composites

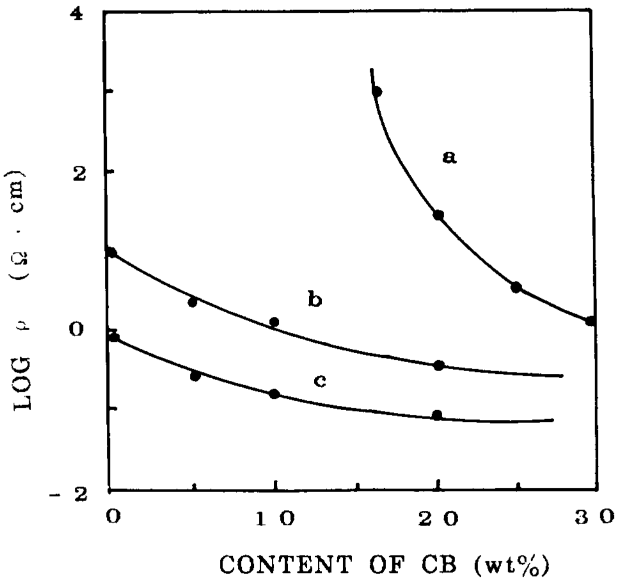

Figure 4 Variation of the resistivity of the composites mixed by the solvent method with CB content when CF content is fixed: (a) no CF; (b) 5% CF; (c) 10% CF.

mixed by the Brabender; the fixed CB content of curves a, b, and c is 0, 5%, and 10%, respectively. These two figures show that if CB content is fixed the resistivity of the composites decreases with the increase of CF content.

Therefore, for the composites mixed with CF and CB, from Figures 4–7, it can be concluded that if one of the filler contents (CF or CB) is fixed, increase

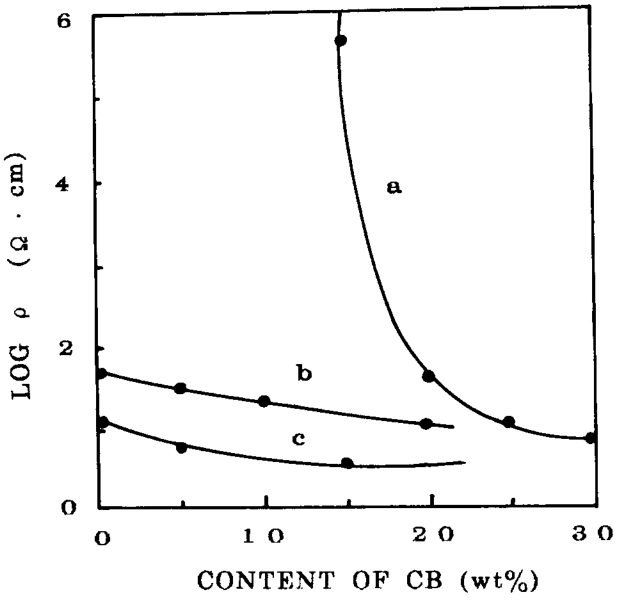

Figure 5 Variation of the resistivity of the composites mixed by a Brabender with CB content when CF content is fixed: (a) no CF; (b) 10% CF; (c) 15% CF.

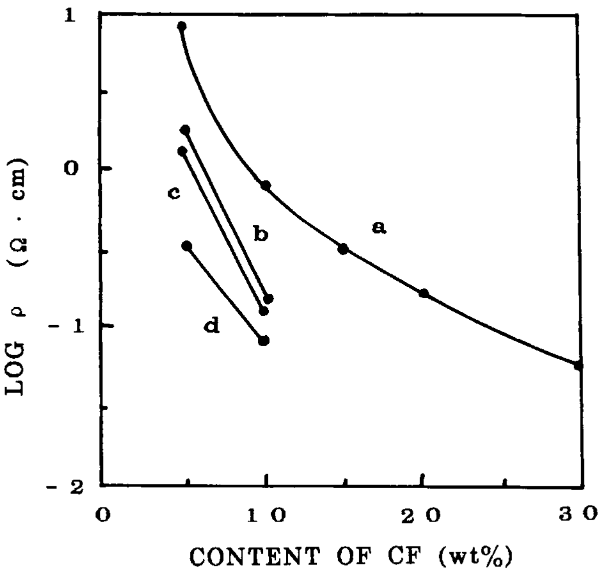

Figure 6 Variation of the resistivity of the composites mixed by the solvent method with CF content when CB content is fixed: (a) no CB; (b) 5% CB; (c) 10% CB; (d) 20% CB.

of the content of the other can directly lead to a decrease of the resistivity of the composites. A comparison of the slope of the curves in Figures 4 and 6 with Figures 5 and 7 indicates that the variation of the resistivity of the composites with CF content if CB content is fixed is greater than that with CB content if CF content is fixed.

From all the discussions above, we can conclude that the main factor to determine the conductivity of the composites mixed with CF and CB is the content of CF. Also, content of CB lower than 10% can decrease the resistivity of the composites filled with CF obviously, but if beyond 10%, the resistivity of the composites varies slightly due to the lower slope of the curves in Figures 4 and 5.

Conduction Mechanism of CF/ABS Resin Composites Mixed with CB

The general theory to explain the conduction mechanism of fibers or particle-filled polymer composites is the "theory of conductive paths,"[5,6] which suggests that it is the existence of conductive paths (fibers or particle contacts) that results in the conductivity of the composites. With increase of the content of the fibers or the particles, conductive paths among the fibers or the particles increase, and the average distance between the fibers or the particles becomes smaller; thus, the resistivity of the composites decreases.

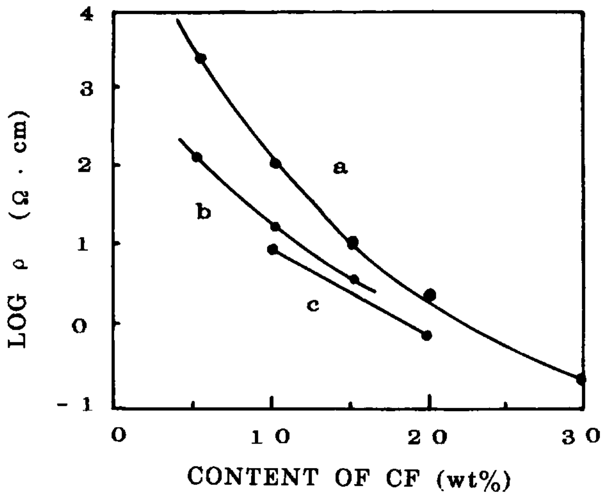

Figure 7 Variation of the resistivity of the composites mixed by a Brabender with CF content when CB content is fixed: (a) no CB; (b) 5% CB; (c) 10% CB.

We use this theory to explain the conduction mechanism of CF/ABS resin filled with CF and CB. Figure 8 is a schematic illustration of the conduction mechanism of this kind of composite. CB are conductive particles; their average size is 60–70 nm. After CB are mixed in CF-filled composites, CB was dispersed in the areas where fibers were not contacted. This makes the fibers have contact with each other or decreases the average distance between the

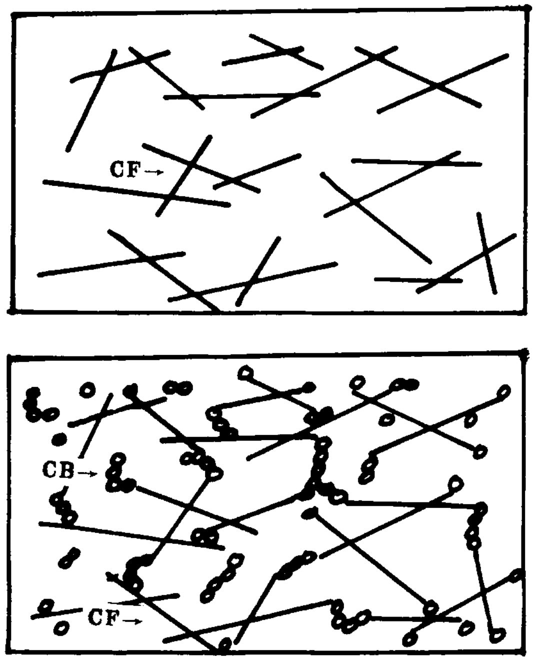

Figure 8 Schematic illustration of the conduction mechanism of the composites filled with CF and CB: (a) filled with CF only; (b) filled with both CF and CB.

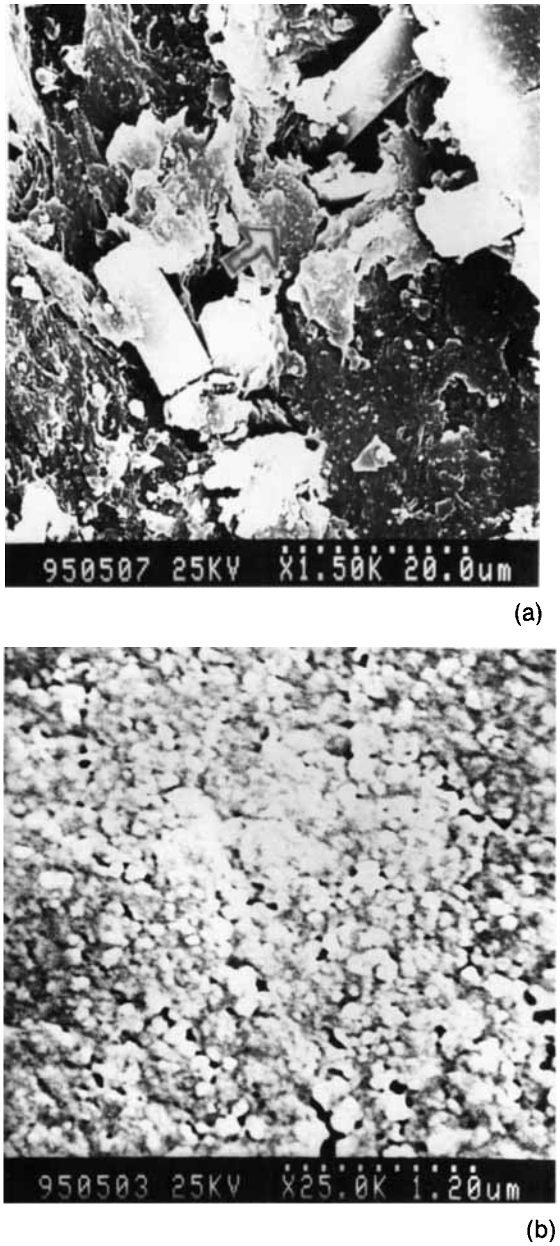

Figure 9 SEM microphotographs of the cross section of the composites filled with CF and CB by the Brabender; the filler content is 15% (CF: 10%, CB: 5%), (a) is enlarged 1500 times, and the place which the arrowhead points to was then enlarged 25,000 times, as (b) shows.

fibers; thus more conductive paths in the composites are formed, which leads to the decrease of the resistivity of the composites. The more CB particles filled in the composites, the more conductive paths have been formed. But if the content of CB is filled, a conductive network has been formed in the composites; then, increasing the content of CB can only slightly increase the conductive paths. The small decrease of the resistivity of the composites is almost completely due to the increase of CB content and has a little relation with CF. This explains why in Figures 4 and 5 when CB content is higher than 10% the variation of the resistivity of the composites is roughly steady.

Figure 9 shows SEM microphotographs of the composites filled with 15% filler content (CF: 10%, CB: 5%). Figure 9(a) is enlarged 1500 times; the bright cylindric part is CF and the rest is ABS resin mixed with CB. The place to which the arrowhead points in (a) was enlarged 25,000 times, as Figure 9(b) shows, in which the bright spots are CB particles, whose average size is 60–70 nm. Just as Figure 8 indicates, the SEM microphotographs prove that CB particles disperse among the fibers in the composites, increase the conductive paths, and thus decrease the resistivity of the composites.

According to the "theory of conductive paths," the more conductive paths in the composites, the better is the conductivity of the composites. The fibers are very thin; their diameter is only 7 μm. By the method introduced in the Experimental part, the fiber aspect ratio of the composites mixed by the solvent method is about 600, i.e., the fibers' length is about 4 mm, which indicates that by being mixed by this method the fibers have been slightly damaged, and the fiber aspect ratio of the composites mixed by the Brabender is about 40, i.e., the fibers' length is 0.3 mm. Fibers have enough length whichever mixing method is used, so when mixed in the composites, they are easy to have contact with each other and form the conductive paths. However, CB particles are very fine; their diameter is only 60–70 nm (0.06–0.07 μm). When mixed in the composites, obviously it is much more difficult for them to contact with each other than with CF and thus they form much fewer conductive paths. So, the conclusions are the same with the discussions in the first part in that the main factor to determine the conductivity of the composites filled with CF and CB is the content of CF, and if the composites are filled only with CB, it is difficult for resistivity of the composites to be lower than 1 Ω cm.

Possibility of Using CB as a Substitute for Part of CF in the Composites to Decrease the Production Cost

Table I shows a comparison of the resistivity of the composites filled with CF and CB with that of the composites filled with CF only. It is shown in Table I that if 5% CF is substituted by CB in CF-filled composites the resistivity of the composites before

Table I Comparison of the Resistivity of the Composites Mixed with CF and CB with That of the Composites Mixed with CF Only

Mixing Method	Total Content	CF Content	CB Content	Resistivity (Ω cm)	CF Content[a]	Resistivity (Ω cm)[b]
Solvent method	7%	5%	2%	5.0×10^0	6.3%	3.2×10^0
	10%		5%	2.4×10^0	8%	9.8×10^{-1}
	15%		10%	1.0×10^0	10%	2.3×10^{-1}
	25%		20%	3.9×10^{-1}	13%	6.3×10^{-2}
	15%	10%	5%	2.8×10^{-1}	14%	2.3×10^{-1}
	20%		10%	1.6×10^{-1}	17.5%	1.0×10^{-1}
	30%		20%	7.9×10^{-2}	22.5%	5.2×10^{-2}
Brabender	15%	10%	5%	2.5×10^1	13.5%	1.3×10^1
	20%		10%	1.7×10^1	14.5%	2.2×10^0
	30%		20%	9.1×10^0	15.5%	2.2×10^{-1}
	20%	15%	5%	5.9×10^0	17%	2.2×10^0
	25%		10%	4.0×10^0	18%	6.3×10^{-1}
	30%		15%	3.1×10^0	18.5%	2.2×10^{-1}

[a] CF content needed to reach the same resistivity with the composites mixed with both CF and CB.

[b] Resistivity of the composites mixed with CF only, and the CF content is the same with the total content of CF and CB.

substitution is roughly the same as that after substitution; but if the substituted CF content is greater than 5%, the difference between the resistivity of the composites before and after substitution cannot be ignored. For example, in considering the composites mixed by the solvent method, if the total filler content is 10% (CF: 5%, CB: 5%), the resistivity of the composites is 2.4×10^0 Ω cm, and if 10% CF is filled, the resistivity of the composites is about 1 Ω cm. The resistivity of the two composites is approximately the same. However, if the total filler content is 25% (CF: 5%, CB: 20%), the resistivity of the composites is 3.9×10^{-1} Ω cm, and if 25% CF is filled, the resistivity of the composites is about 6.3×10^{-2} Ω cm. The difference between them is beyond one order of magnitude. Similarly, considering the composites mixed by the Brabender, if the total filler content is 20% (CF: 15%, CB: 5%), the resistivity of the composites is 5.9×10^0 Ω cm, and if 20% CF is filled, the resistivity of the composites is about 2.2×10^0 Ω cm. However, if the total filler content is 25% (CF: 15%, CB: 10%), the resistivity of the composites is 4.0×10^0 Ω cm, and if 25% CF is filled, the resistivity of the composites is about 6.3×10^{-1} Ω cm. The difference between them is also beyond one order of magnitude.

On the other hand, from the CF content needed to fill the composites to reach the same resistivity with that of the composites filled with CF and CB, the above conclusion can also be made. For example, if mixed by the Brabender, the total content is 15% (CF: 10%, CB: 5%), the resistivity of the composites is 2.5×10^1 Ω cm; to reach the same resistivity if only CF is filled, the CF content needed to be filled in the composites is 13.5%. The two fillers' content is approximately the same, but if the total content is 20% (CF: 10%, CB: 10%), the resistivity of the composites is 1.7×10^2 Ω cm to reach the same resistivity, and if only CF is filled, the CF content needed to be filled in the composites is 14.5%. The difference between them is 5.5% and cannot be ignored.

If only CB is filled in the composites, not only the conductivity but also the mechanical properties of the composites cannot satisfy the demand of applications. CF has high strength, so filling CF in the composites can have a significant reinforcing effect. But more CF means more production cost due to the high price of CF. CB's price is very low. From the above discussion, using CB as a substitute for the part of CF in the composites can decrease the production cost; in the meantime, the conductivity of the composites before and after substitution is approximately the same. When CF content is higher than 10%, the optimum substitution amount of CB for CF cannot be beyond 5%. When CF content is lower than 10%, the optimum substitution amount of CB for CF should be smaller, such as 1–2%; otherwise, CF content will be so small that it will influence the mechanical properties of the composites, and on the other hand, the conductivity of the composites with too small CF content cannot be adequate even if the CB are filled. For example, considering the composites mixed by the solvent method, if the total filler content is 7% (CF: 5%, CB: 2%), the resistivity of the composites is 5.0×10^0 Ω cm, and if 7% CF is filled, the resistivity of the composites is about 3.2×10^0 Ω cm and the CF content needed to reach the same resistivity is 6.3%.

However, of course, filling CB in the composites will influence the mechanical properties such as tensile strength, but it is less important than to decrease the production cost. Research of this aspect will be done in the future.

CONCLUSIONS

From the discussion above, the following conclusions can be made:

1. The resistivity of the composites filled with CF, CB, or both CF and CB decreases with increase of the filler content. For the same filler content, the greater the CF proportion in the fillers, the lower is the resistivity of the composites. Also, if only CB is filled, it is difficult for the resistivity of the composites to be lower than 1 Ω cm. The main factor needed to determine the conductivity of the composites mixed with CF and CB is the content of CF. The content of CB lower than 10% can obviously decrease the resistivity of the composites filled with CF, but if beyond 10%, the resistivity of the composites varies slightly.
2. Using CB as a substitute for part of CF in CF-filled composites can decrease the production cost and hardly change the conductivity of the composites. The optimum substitution amount of CB for CF is 5% when CF content of the composites before substitution is beyond 10%, and when CF content is lower than 10%, the optimum substitution amount of CB for CF should be smaller, such as 1–2%.

The authors are very grateful to Dr. Wentao Jia, Department of Materials Science, Jilin University, People's Republic of China, for providing the carbon blacks and for other support of this work.

REFERENCES

1. Z. Q. Baker, M. K. Abdelazeez, and A. M. Zihlif, *J. Mater. Sci.*, **23,** 2995–3000 (1988).
2. P. B. Jana, A. K. Mallick, and S. K. De, *Composites,* **22**(6), 451–455 (1991).
3. J.-M. Chiou, Q. Zheng, and D. D. L. Chung, *Composites,* **20**(4), 379–381 (1989).
4. P. B. Jana, S. K. De, S. Chaudhuri, and A. K. Pal, *Rubb. Chem. Technol.*, **65,** 7–23.
5. S. Miyauchi and E. Togashi, *J. Appl. Polym. Sci.*, **30,** 2743–2751 (1985).
6. M. H. Polley and B. B. T. Boonstra, *Rubb. Chem. Technol.*, **30,** 170–180 (1957).

Received November 3, 1995
Accepted June 10, 1996