

Melt Viscosity and Electrical Conductivity of Carbon Black-PVC Composite

TSUTOMU NOGUCHI, TOHRU NAGAI, and JUN'ETSU SETO, *Sony Corporation Research Center, 174 Fujitsukacho, Hodogaya-ku, Yokohama, 240 Japan*

Synopsis

The effect of the structure of carbon black aggregates on the melt behavior and electrical conductivity of carbon black-vinylchloride-vinylacetate copolymer systems was analyzed. As the amorphous carbon aggregates are roll-milled, they become cylindrical, then, as the milling time is prolonged, spherical. During milling, polymer adsorption and dispersivity increases in the same manner, causing the viscosity of the composite to decrease. It was established that during a certain milling time, conductivity rises to a peak, after which it falls. We attribute this phenomenon to there being an optimum aspect ratio and degree of dispersion of the cylindrical carbon aggregates. A model explaining the relationship between milling time and change in conductivity is proposed. When oxidized carbon black was dispersed into the copolymer, it was found that it disperses better than unoxidized carbon black, although the conductivity of the resulting composite is lower.

INTRODUCTION

The relation between the dispersion of carbon black in composites and the physical and electrical properties of these composites has been extensively studied in rubber-carbon black systems.^{1,2} This relationship is not yet fully understood in carbon black with extremely large specific surface area thermoplastic composite systems, however. Fox³ has reported conductivity and melt flow behavior of carbon black-polyvinylchloride (PVC) composite as a function of weight percent loading. Kawamoto⁴ reported ac conductivity measurements and discussed the composites' conduction mechanism.

Conductive polymer composites in which conductive filler has been dispersed into the base material is finding increasing application in electronic components. Carbon black-polyvinylchloride composite is now being used for the capacitive video disc, for example.⁵ In this application, the composite used must not only be capable of being molded into submicron pits, but it also must have an electrical conductivity of over $10^{-1} \Omega^{-1} \text{cm}^{-1}$.

In order to achieve this degree of moldability and conductivity, the composite must have a high carbon black content, but a high carbon black content means decreased processability. To determine the optimum milling conditions, it is necessary to study the effect of the structure of the carbon black aggregates on the melt behavior and electrical conductivity of the system. In this report, the melt flow behavior and electrical conductivity of carbon black-polyvinylchloride systems are investigated and explained in terms of the structure of carbon black aggregates.

EXPERIMENTAL

Materials

The resin used was vinyl chloride-vinyl acetate copolymer purchased from Shinetsu Kagaku Co. Ltd. Its properties are given in Table I. The carbon black used was manufactured by Akzo Chemie Ltd. Figure 1 is a scanning electron micrograph of the carbon black particles. The particles' characteristics are summarized in Table II. 5 wt% of dibutyl-tin-dilaurate was added as a heat stabilizer.

Composite Preparation

Composites with different filler content were blended at 160°C in a roller mill for 5 to 60 min. Discs about 2 ± 0.2 -mm thick were molded from the mixtures at 150°C. Reduction of the molecular weight by thermal degradation did not occur during the mixing.

Melt viscosity

Melt viscosity was measured using a capillary rheometer in the same way as in the previous study.⁶ The measurement was carried out at 170°C.

Electrical Conductivity

The equipment used to measure electrical conductivity was a Yokogawa-Hewlett-Packard 192A LF impedance analyzer. The specimens were 55 mm in diameter and about 2 ± 0.2 mm thick. Gold was vacuum-deposited on the surface of the specimens. Measurements were performed at 100 kHz in a dry atmosphere at 25°C, using the electrode shown in Figure 2.

Viscoelasticity

Viscoelasticity was measured with a Rheovibron III EA apparatus from Toyo Baldwin Co. Ltd. at 110 Hz. The heating rate was 1°C/min.

Determination of Adsorbed Polymer

Measurements were carried out by a Soxhlet extractor with tetrahydrofuran (THF) for 24 h. Composites were packed in cylindrical filter paper (No. 86R, supplied by Toyo Roshi Co. Ltd.), then the polymer undissolved in THF was weighed.

TABLE I
PVC Resin Sample

\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n	Tg	Content of vinylacetate
7.9×10^4	3.6×10^4	2.19	77°C	12.5%

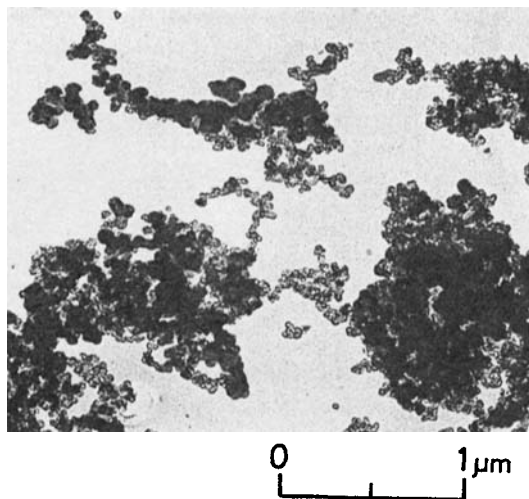


Fig. 1. Scanning electron micrograph of carbon black.

Surface Treatment

The carbon black was boiled in a $\text{KMnO}_4\text{-HNO}_3$ solution for 2 h. The resulting oxidized carbon black was washed in distilled water several times to remove the nitric acid, then dried at 120°C *in vacuo*.

RESULTS AND DISCUSSION

Melt Viscosity

Figure 3 shows the relationship between the melt viscosity and the shear rate of composites with various filler contents. As can be seen, the PVC resin exhibits Newtonian flow behavior below a shear rate of 10 sec^{-1} . As the shear rate increases, non-Newtonian flow behavior appears. This phenomenon can be explained by the reduction of the volume of the segmental flow unit. As the carbon black content is increased, the viscosity increases, with the greater effect at low shear rates. This behavior probably originates from the increase in "structural viscosity" caused by the forming of the carbon black aggregates. In the high shear rate region, however, the increase in viscosity is less pronounced, due to the rupturing of the carbon black aggregates. For a carbon black content of 15 wt%, the milling time was varied from 10 to 60 min, with the result that the melt viscosity de-

TABLE II
Carbon Black Sample

Average diameters	Surface area ^a	Density ^b	Shape
300 Å	1000 m ² /g	2.069 g/cc	Spherical

^aBET method.

^bPycnometer method.

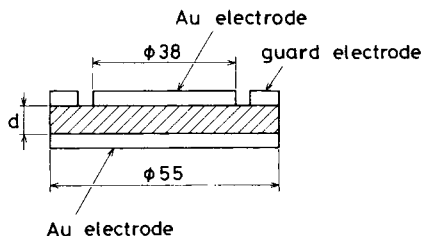


Fig. 2. Dimensions of an electrode.

creased as the milling time increased. This phenomenon is particularly noticeable at low shear rates and is also related to the decrease in the size of the carbon black aggregates.

Electrical Conductivity

Figure 4 is a plot of electrical conductivity versus carbon black content. As can be seen, the electrical conductivity increases as the carbon black content increases. Note the drastic increase between 5 and 10 wt%. We found that the carbon black content must be about 15 wt% in order for the composite material to have the conductivity of $10^{-1}\Omega^{-1}\text{cm}^{-1}$, which is necessary for a capacitive video disc application.

Figure 5 shows the relation between the electrical conductivity and milling time for a carbon black content of 15 wt%. The relationship between milling time and melt viscosity is also shown. It is interesting to note that the electrical conductivity increases until 30 min of milling time, after which it decreases. It is clear that the optimum milling time must be determined in order to obtain maximum conductivity.

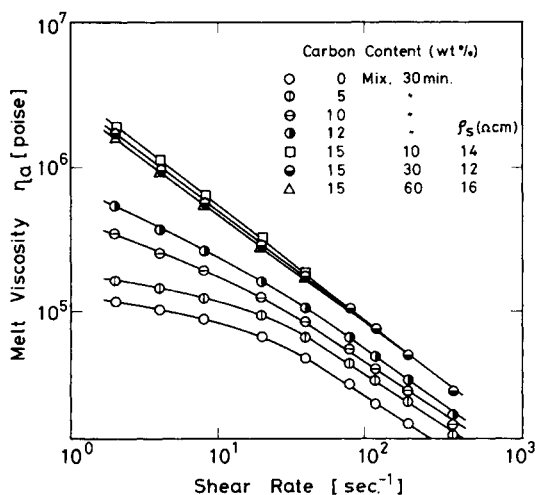


Fig. 3. Flow curve of carbon black-PVC composites.

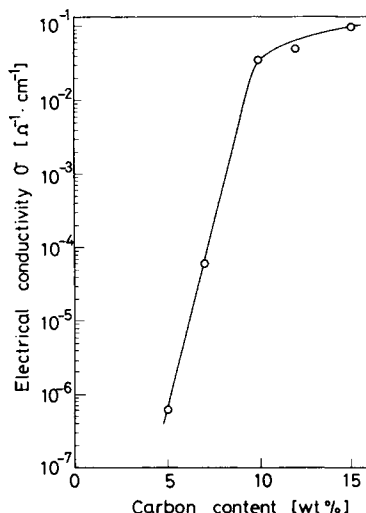


Fig. 4. Electrical conductivity versus carbon content.

Viscoelasticity

Figure 6 shows the dynamic modulus E' and loss modulus E'' versus temperature for a composite whose carbon content is 15 wt% and for a polymer with no filler. Note that glass transition temperature (T_g) of the composite shifts to a significantly higher temperature ($=76^\circ\text{C}$) as compared with that of the polymer without filler ($=70^\circ\text{C}$).

It has been previously reported⁷ that there is also a rise in T_g for the same polymer system containing an oleate monomolecular layer-coated α -hematite powder. This result was attributed to the formation of a stronger interchain bonding between acetate groups. The same explanation could be applied to the present system. The hydrophobic property of the carbon black surface would tend to orient the acetate groups toward the outside. This would increase the interaction among the acetate groups of the polymer, resulting in a T_g shift toward higher temperatures.

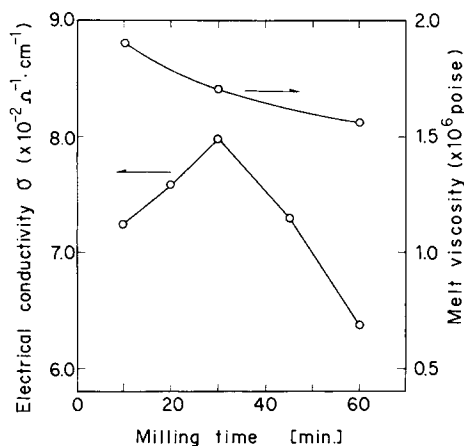


Fig. 5. Relation among milling time, electrical conductivity, and melt viscosity.

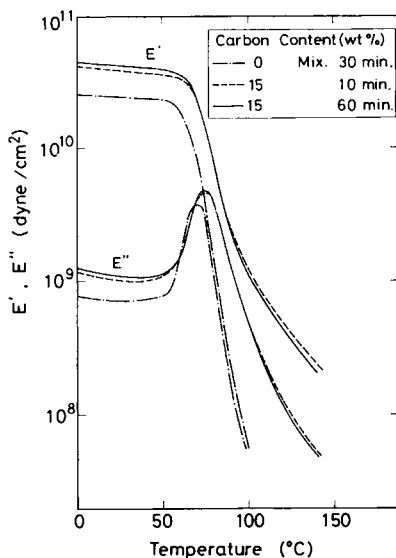


Fig. 6. Viscoelastic property of carbon black-PVC composite.

In the case of the composite containing oxidized carbon black, T_g should be shifted to a lower temperature, because its surface is hydrophilic. This result will be described in a later section entitled "Effect of Surface Oxidation of Carbon Black".

Dynamic modulus E'_c corrected by the porosity ψ calculated by Eq. (1), and the theoretical value calculated by Guth-Gold's equation are listed in Table III.

$$E'_c = \frac{E'}{1 - \psi} \quad (1)$$

The measured values in the glassy region increase with milling time, and are larger than the calculated values. This difference may be caused by the adsorption of polymer onto the surface of the carbon black.

Effect of Polymer Adsorption

The amount of polymer adsorption per gram of carbon black, A_p (g/g) is obtained by measuring the weight of the polymer in the composite before and after Soxhlet extraction. The results of the measurement are shown

TABLE III
Dynamic Modulus of Carbon Black-PVC Composites

Milling time (min)	Porosity	Measured, E' (dyne/cm ²)	Calc'd by Eq. (1) (dyne/cm ²)	Calc'd by Guth eq. (dyne/cm ²)
10	2.1%	3.42×10^{10}	3.49×10^{10}	3.51×10^{10}
30	1.1%	3.49×10^{10}	3.53×10^{10}	
60	0.9%	4.09×10^{10}	4.13×10^{10}	

$$E/E_0 = 1 + 2.5 \phi + 14.1 \phi^2$$

E : dynamic modulus of composite.

E_0 : dynamic modulus of matrix.

ϕ : volume fraction of filler.

in Figure 7. A_p increases sharply until milling time reaches 30 min, after which the increase is more gradual.

From the scanning electron micrograph of carbon black aggregates which is shown in Figure 8b and c, if we assume that the aggregates are, respectively, cylindrical and spherical, we can calculate the apparent surface area per gram of carbon black aggregates. We find that the amount of polymer adsorption per square meter of surface area of the carbon black aggregates is 74 mg/m^2 and 76 mg/m^2 , as is shown in Figure 7. As can be seen, this value undergoes little change as A_p increases. Consequently, we can state that the increase in A_p is brought about by an increase in the surface area per unit weight of the aggregates as the milling time increases. Or, put another way, A_p has good correspondence with the change in the degree of dispersion.

Microscopic Observation of Carbon Black Aggregates

Figure 8 shows scanning electron micrographs of the residual composite after THF-soluble polymer in the composite has been extracted with a Soxhlet extraction apparatus. As can be seen, the carbon black aggregates are irregular in shape until they have been milled for about 10 min, and their length is widely distributed from 0.8 to $9 \mu\text{m}$ (Fig. 8a). As milling time increases, the aggregates become cylindrical (Fig. 8b). Then the cylindrical aggregates rupture to become smaller spherical aggregates as milling is prolonged (Fig. 8c).

Effect of Size and Shape of Carbon Black Aggregates

As was previously stated,⁷ the adsorbed polymer has a higher glass-transition temperature T_g than that of bulk polymer, and therefore the dynamic modulus and melt viscosity increase because of the loss of flexibility of the polymer chain adsorbed on the filler.

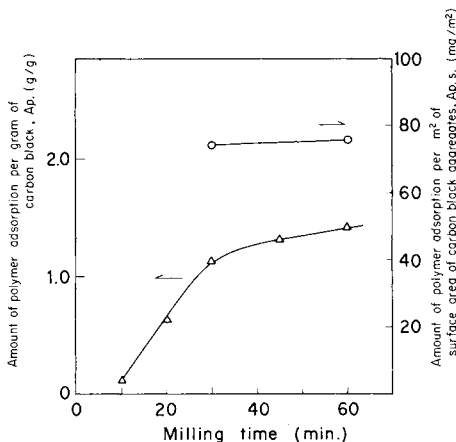


Fig. 7. Relation between milling time, A_p , and $A_{p.s.}$

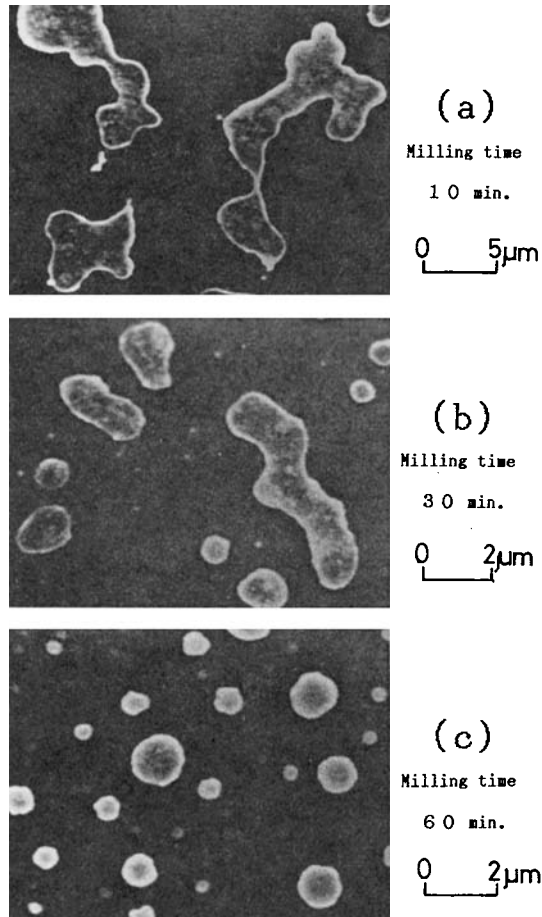


Fig. 8. Scanning electron micrographs of carbon black aggregates.

The effective volume fraction of the filler with adsorbed polymer ϕ_e can be expressed as in Eq. (2).

$$\phi_e = \phi + \phi_{Ap} \quad (2)$$

For a composite of 15 wt% of carbon black content (which equals 11 vol%) which has been milled for 60 min, the volume fraction of adsorbed polymer ϕ_{Ap} is 22 vol%, and ϕ_e of calculated value is 33 vol%. ϕ_e increases three times as much as the volume fraction of filler with milling time.

Brennan⁸ and Pliskin et al.⁹ reported that the melt viscosity increases as the amount of adsorbed polymer increases for rubber-carbon black systems. Our results, however, indicate that the melt viscosity in our system decreases almost linearly from 1.90×10^4 to 1.55×10^4 poises as the amount of adsorbed polymer is increased from 2.1 to 22 vol%. It would seem that "structural viscosity" makes a greater contribution to melt viscosity than the increase in the apparent melt viscosity that is caused by the rupturing of large aggregates into fine spherical particles and increasing the amount of adsorbed polymer.

The change in electrical conductivity during the milling process is related to the distance between aggregates, which changes as the shape of the aggregates changes.

The typical shape and dimensions of the aggregates were determined by taking electron micrographs of the aggregates and analyzing the results with an image analyzer. The results are shown in Table IV together with the distance between aggregates obtained by our model analysis. If we assume the cylindrical aggregates to be aligned longitudinally, the length of conductive aggregates per unit length of the composite changes with milling time, as is shown in the table. The conductive path is longest when the milling time is 30 min, demonstrating that the aspect ratio of the cylindrical carbon black aggregates at 30 min of milling time is highest. It should be stressed that the electrical conductivity at 30 min of milling time is at a maximum.

We believe that the decrease in electrical conductivity which occurs as milling time is prolonged beyond 30 min is brought about by the electrical conductive path's being cut short by the rupturing of the cylindrical aggregates into the smaller spherical aggregates shown in Figure 8c.

Effect of Surface Oxidation of Carbon Black

We investigated the effect of the surface oxidation of carbon black which is intended to improve the dispersion of the particles.

The polymer adsorption on the oxidized carbon black which is found in THF solution is 25% larger than that of unoxidized carbon black. These values were measured by the viscosity method. The increase in the polymer adsorption caused by this treatment is due to the formation of polar groups, which increase the affinity between the particles' surface and the acetate groups in the polymer chains. The polar groups, such as the -COOH, -OH, etc., formed on the particles' surface were generated during the oxidation process. Indeed, the pH of the unoxidized and oxidized carbon black is 8.4 and 4.7, respectively.

The Tg of the composite containing oxidized carbon black is 2°C lower than that containing unoxidized carbon black. As described previously, this may be due to the oxidized carbon black's surface becoming more hydrophilic, and the acetate groups orientating toward the carbon black's surface,

TABLE IV
The Model Analysis of Distance between CB Aggregates

Milling time (min)	Shape of CB aggregate	Average dimensions of CB aggregate	Packing model	$L_{CB} \cdot L_{CB} + T_{PVC}^b$
10	Cylindrical	Length: 2.6 μm	Cubic	0.68
		Diameter: 1.7 μm	Rhombohedral	0.60
30	Cylindrical	Length: 1.1 μm	Cubic	0.71
		Diameter: 0.7 μm	Thomohedral	0.63
60	Spherical	Diameter: 0.7 μm	Cubic	0.58
			Rhombohedral	0.52

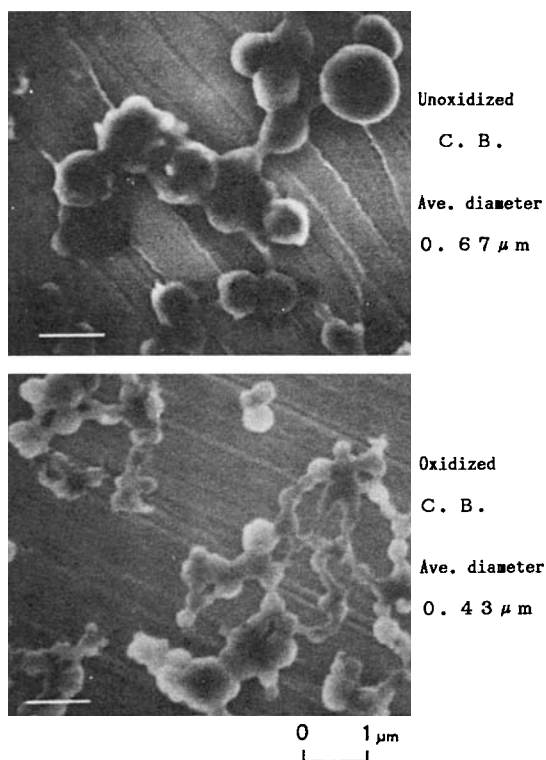


Fig. 9. Scanning electron micrographs of unoxidized and oxidized carbon black.

which result in a decrease in the concentration of acetate groups in the resultant polymer layer which lowers the T_g .

In order to compare the physical behavior of composites employing oxidized carbon black with those containing unoxidized carbon black, these same experiments were carried out with oxidized carbon black filler. Figure 9 compares the scanning electron micrographs of oxidized and unoxidized carbon black aggregates. As can be seen, the oxidized carbon black aggregates are smaller. Figure 10 also compares the melt viscosity versus the shear rate of unoxidized and oxidized carbon black. With oxidation, the melt viscosity of composites dispersed with oxidized carbon black is 20% lower, resulting in improved processability. These results indicate that oxidized carbon black aggregates are more readily dispersed in a polymer. Electrical conductivity of a composite dispersed with oxidized carbon black, however, is one order of magnitude lower than that of a composite dispersed with unoxidized carbon black, as is shown in Figure 11. As we know that the electrical conductivity of oxidized and unoxidized carbon black is $4\Omega^{-1}\text{cm}^{-1}$ and $10\Omega^{-1}\text{cm}^{-1}$, respectively, we can attribute the one order of magnitude decrease of electrical conductivity found in composites to the superior dispersivity of oxidized carbon black filler.

CONCLUSION

The melt flow behavior and electrical conductivity of a carbon black-polyvinylchloride (PVC) system were analyzed in terms of the structure of carbon black aggregates.

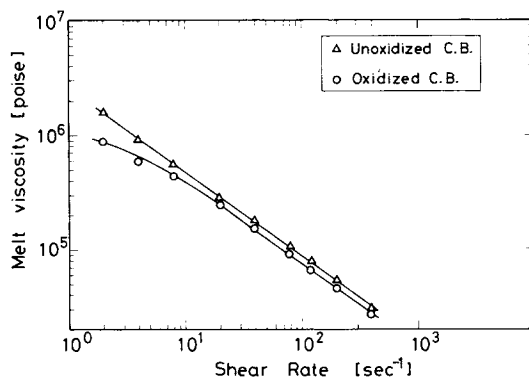


Fig. 10. Flow curve of composites containing unoxidized and oxidized carbon black.

It was found that the melt viscosity decreased with milling time. During the milling process, carbon black aggregates first became cylindrical in shape, then ruptured to become small spheres. The amount of polymer adsorption A_p increased as the apparent surface area of the carbon black aggregates increased. That is, A_p has a good correspondence with the degree of dispersion. The decrease of melt viscosity was caused by a decreased "structural viscosity," because the larger aggregates were ruptured by milling and well dispersed in the polymer matrix.

On the other hand, the electrical conductivity increased, going through a maximum, then decreasing as the aggregates were broken up into fine spherical particles. This phenomenon was the result of the optimum aspect ratio of the cylindrical carbon black aggregates being realized at the point of maximum conductivity. This relation was elucidated by an analysis of a model of the distance between aggregates. The decrease in electrical conductivity was brought about by the electrical conductive path's being cut short. This was caused by the cylindrical aggregates' rupturing into smaller spheres.

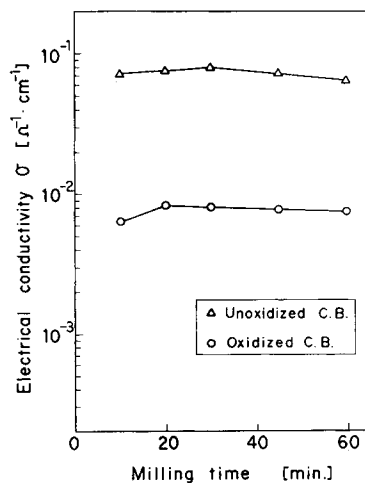


Fig. 11. The effect of surface oxidation of carbon black on electrical conductivity.

The oxidized carbon black had a larger affinity with PVC than the unoxidized carbon black, resulting in better dispersion. The electrical conductivity decreased because of the decrease in the electrical conductivity of the oxidized carbon black.

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