

Electrical Characteristics of Fluorinated Carbon Black-Filled Poly(vinylidene fluoride) Composites

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ABSTRACT: Dispersion and electrical properties of fluorinated carbon black-filled poly(vinylidene fluoride) (PVDF) composites were studied as a function of the fluorine content. It was found that with increasing the fluorine content carbon particles tend to stick together to form large aggregates. The percolation concentration increases to a high concentration, whereas the percolation process becomes gradual. The temperature dependence of resistivity measurements show that the fluorinated carbon black-filled PVDF composites exhibit a high PTC intensity and a low NTC effect. These phenomena were discussed in terms of thermodynamic interactions between fluorinated carbon and the PVDF matrix. The dielectric behavior was also investigated in this study. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1063–1070, 2001

Key words: fluorination; carbon black; poly(vinylidene fluoride); conductive polymer composites

INTRODUCTION

Fluorinated carbon black (FCB) has recently been fabricated to be a new class of reinforcing or conducting filler.^{1–3} By reacting carbon black with elemental fluorine via proprietary processes, both surface energy and electrical conductivity of carbon black can be adjusted due to a layer with strong carbon–fluorine (C–F) covalent bonds at the surfaces.^{4–7} It was reported^{2,7} that fluorinated graphite has a surface energy in the range 38–47 mJ/m², which is less than one-third that of graphite. The conductivity of FCB increases at low F/C atomic ratios due to the ionic nature of the C–F bond,^{1,4} then decreases as the fluorine content further increases.

The objective of this work was to clarify the effect of the fluorine content of carbon black on

the dispersion and electrical properties of filled polymer composites. It was expected that the reduction in the carbon black's surface energy by fluorination may reduce the interfacial free energy between FCB and the polymer and thus improves their wettability, since the surface energy for most polymers is very low within the range of 35–45 mJ/m².⁸ Poly(vinylidene fluoride) (PVDF) was selected as a matrix not only because of the interesting electric characteristics but also due to its potential of high affinity to FCB.

EXPERIMENTAL

Four kinds of FCB with a F/C atomic ratio of 0, 0.10, 0.14, and 0.25 (from Daikin Industries, Ltd.) were used as a conductive filler. They are designated as F-0, F-0.10, F-0.14, and F-0.25, respectively. Some of their physical characteristics are listed in Table I. Prior to mixing, both the carbon particles and poly(vinylidene fluoride) (PVDF)

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Table I Characteristics of Carbon Powders Used

	F-0	F-0.10	F0.14	F0.25
F/C atomic ratio ^a	0.00	0.10	0.14	0.25
Particle diameter (nm)	42	42	42	42
Nitrogen surface area (m ² /g)	740	660	640	610
DBP ^b adsorption number (mL/100 g)	460	450	440	420
Iodine adsorption (mg/g)	780	600	570	550
Crystalline thickness ^c L_a (nm)	4.03	—	—	3.92

Data from Daikin Industries.

^a By elementary analysis.

^b Dibutyl phthalate.

^c Calculated from Raman spectroscopy measurements.

(Forafon F1000HD from Showa Denko Co.) were dried at 80°C for 24 h under a vacuum. Then, they were mixed together using a two-roll mill for 15 min at 220°C. Sheets with a thickness of about 1.0 mm were compression-molded from the mixtures at 220°C for 10 min under a pressure of 20 MPa, followed by quenching in cold water.

The electrical resistivity was measured by a Keithley 487 picoammeter in the perpendicular direction of the molded sheets. Silver paste was used to ensure good contact of the sample surface with the copper electrodes. Due to no observable deviation from the four-terminal measurements, data in this work were measured using a two-terminal technique under a dc condition. The room-temperature resistivity was measured at room temperature after a wait of 2 min to obtain a stationary value. The temperature dependence of the resistivity measurement was carried out by a computer-controlled system at a heating rate of 2°C/min. Dielectric spectra were determined using an impedance analyzer (4192A Model, Hewlett–Packard) with frequencies from 0.01 kHz to 10 MHz at room temperature.

The dispersion of FCB in the PVDF matrix was observed using a field-emission-type scanning electron microscopy (FE S800, HITACHI). Specimens were fractured in liquid nitrogen. Then, they were etched by the Ar ion for 15 min using an Eiko IB-3 equipment and coated with Pt–Pd. Quantitative analysis of the FCB dispersion was performed by the statistical processing of the SEM photographs using the quadrature method and Morishita's I_δ value.⁹

The I_δ index, which plays an important role in the characterization of the dispersion mode, is given by

$$I_\delta = q\delta \quad (1)$$

with

$$\delta = \frac{\sum_{i=1}^q n_i(n_i - 1)}{N(N - 1)} \quad (2)$$

where q is the number of elemental parts equally divided from the total area of the SEM pattern; n_i , the number of particles in the i th section; and N , the total number of particles:

$$N = \sum_{i=1}^q n_i \quad (3)$$

RESULTS AND DISCUSSION

Dispersion State

The FCB powders utilized in this study were obtained from direct fluorination of conductive carbon blacks at about 400°C. They were characterized by XPS, photoacoustic spectra (PAS), and Raman spectroscopy measurements, confirming¹⁰ that C—F covalent bonds are exclusively formed on the outermost surfaces of FCB particles. Table I contains some of the basic material parameters. As shown, the particle size, DBP adsorption number, and crystallite thickness, L_a , of various FCB powders do not change with an increasing F/C atomic ratio, except for a little reduction of the surface area, indicating that the structural properties of pristine carbon black are maintained in FCBs.

Figure 1(a–d) give SEM micrographs of the various PVDF/FCB composites containing 5 phr FCB. It is shown that the morphology of the

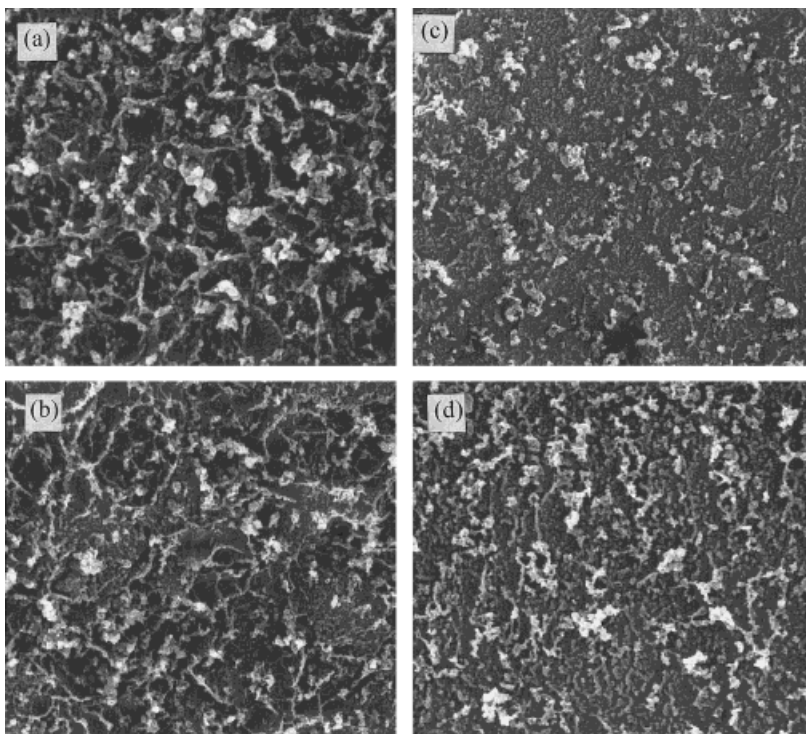


Figure 1 SEM micrographs of PVDF/FCB composites containing 5 phr (a) F-0, (b) F-0.10, (c) F-0.14, and (d) F-0.25.

PVDF matrix changes greatly with the kind of FCB used. A DSC study revealed that the increase of fluorine content at carbon surfaces does not bring about the variation of the melting temperature (about 168°C) and crystalline degree (about 44%) of the PVDF matrix. Dispersion of FCB also changes with the fluorine content of FCB. As seen in Figure 1, the FCB particles seem easy to agglomerate together with increasing fluorine content.

In consideration of the fact that filler distribution plays an important role in the electrical properties of composites, quantitative analysis of the FCB dispersion was performed by imaging analysis of the SEM photographs using the quadrate method and Morishita's I_δ value.⁹ Morishita's I_δ index is one of the most useful quadrate methods, in which the total area of the SEM pattern is divided into small elementary parts with an equal area and the number of the points in each element is calculated. Figure 2 shows schematically the dependence of the I_δ on q for various distribution modes of particles. For Poisson's distribution, I_δ is always unity [Fig. 2(a)]. For the regular mode of distribution, I_δ gradually decreases with an increasing q value [Fig. 2(b)]. For the aggregate mode, I_δ increases as the q value increases

[Fig. 2(c–f)]. The smaller the size of the aggregate, the larger the value of q at which I_δ becomes larger than unity [smaller size of the aggregate: Fig. 2(d,f); larger size of the aggregate: Fig. 2(c,e)]. Furthermore, when the particles are distributed in the regular mode in each aggregate, I_δ has a maximum peak at a certain value of q [Fig. 2(e,f)].

Figure 3 shows the relationship between Morishita's I_δ value and the dividing number q obtained from the SEM photos in Figure 1. The results give detailed information on the FCB particle dispersion. For the pristine carbon black, there is a small peak in the $I_\delta - q$ curves. So, its dispersion pattern is nearly the Poisson's distribution. With increasing the fluorine content, the height of the peak increases and the peak position shifts to a smaller q , indicating that the FCB particles tend to form large-size aggregates. This is the same result as in the SEM observations.

Generally, dispersion of the filler in the polymer matrix must be determined by competing between the particle–particle and the particle–polymer interactions under an optimized processing condition.¹¹ If the particle self-interactions dominate, then the particles tend to stick together and to form large-size aggregates. However, for

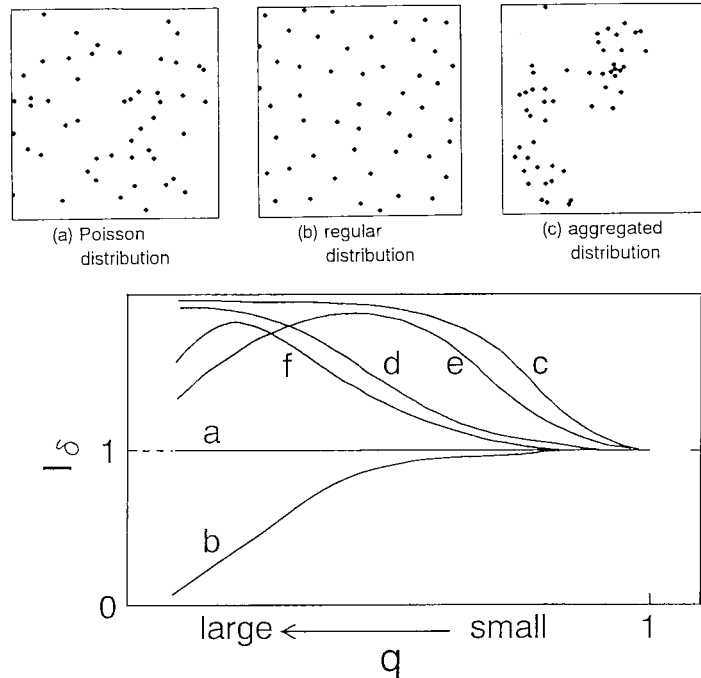


Figure 2 Schematical representation of the relationship between Morishita's I_s value and dividing number q for various distribution modes of particles.

the case of FCB particles, the particle self-interactions should decrease with increasing fluorine content since their surface energy decreases. On the other hand, particle-polymer interactions may be enhanced due to the reduction of the interfacial free energy between FCB and the PVDF matrix. Therefore, the composites filled with

highly fluorinated carbon should be in a better dispersing state, that is, a smaller size of aggregates. Our opposite results might correspond to the nature of difficult dispersion for fluorinated carbon. It should be pointed out that a similar tendency of FCB dispersion was observed both in the nonpolar matrix [low-density polyethylene (LDPE)/FCB] and the polar matrix [poly(methyl methacrylate)/FCB].¹²

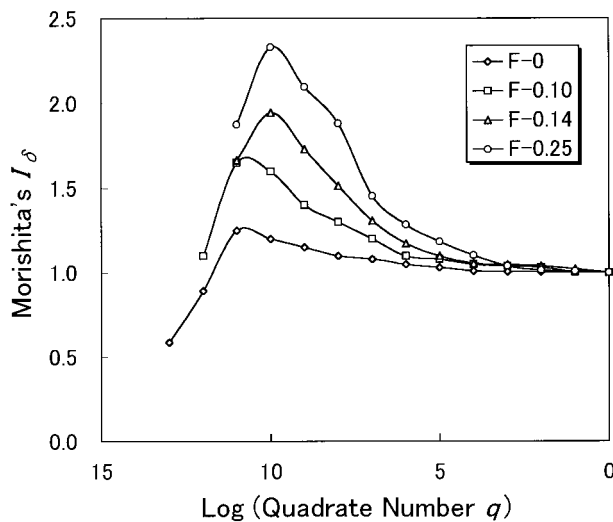


Figure 3 Relationship between Morishita's I_s value and dividing number q for various FCB-filled PVDF composites.

Percolation Behavior

Figure 4 shows room-temperature resistivity of PVDF/FCB composites as a function of filler concentration and fluorine content. Percolation, that is, a large drop in resistivity, takes place for all the PVDF/FCB systems when the filler concentration reaches a particular value, namely, the percolation concentration. After the transitionlike drop, the change in resistivity becomes mild and tends to the same resistivity level for all the FCB/PVDF systems. The percolation concentration is found to increase with the fluorine content from 5 phr for F-0 to 20 phr for F-0.25. Meanwhile, the drop of resistivity at the percolation range becomes gradual. The latter observation demonstrates that the resistivity of composites filled with highly fluorinated carbon black is less sensitive to the filler concentration.

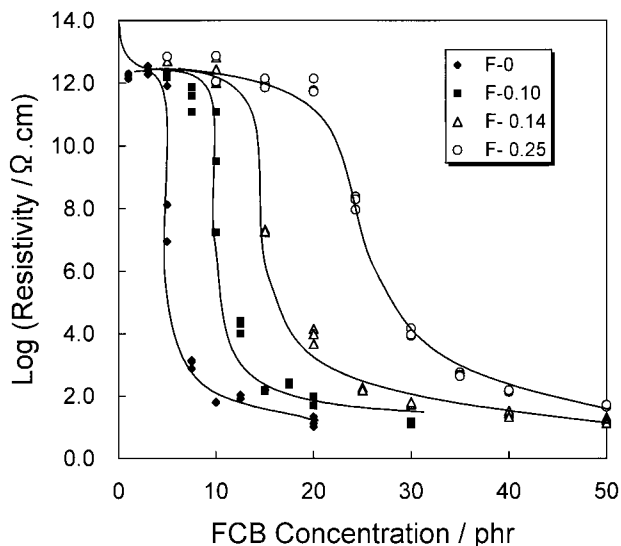


Figure 4 Percolation curves for PVDF/FCB composites as a function of the fluorine content.

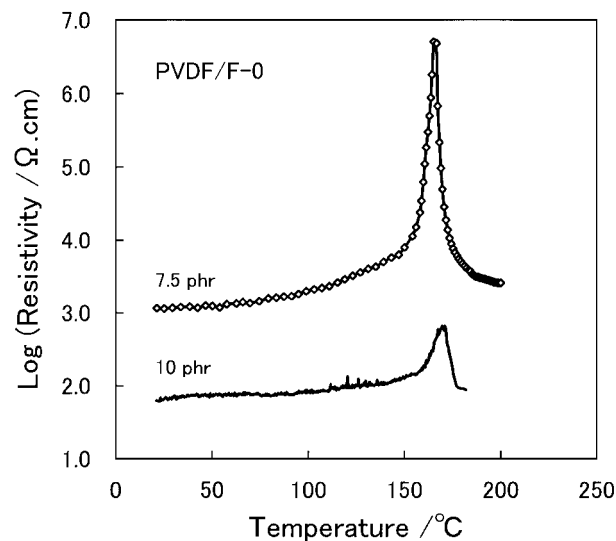
The increase in the percolation concentration with the fluorine content can be understood based on thermodynamic considerations. Generally, incorporation of carbon powders into the polymer matrix will inevitably increase the system energy due to their incompatibility. Miyasaka et al.¹³ proposed that when the total interfacial energy, Δg , between carbon black particles and the polymer matrix reaches a "universal value," Δg^* , the carbon black particles begin to coagulate to form the conductive networks so as to avoid any further increase in system energy, that is, percolation occurs. Since increasing the fluorine content results in decrease of the interfacial free energy between FCB and PVDF, the percolation concentration increases.

Temperature Dependence of Resistivity

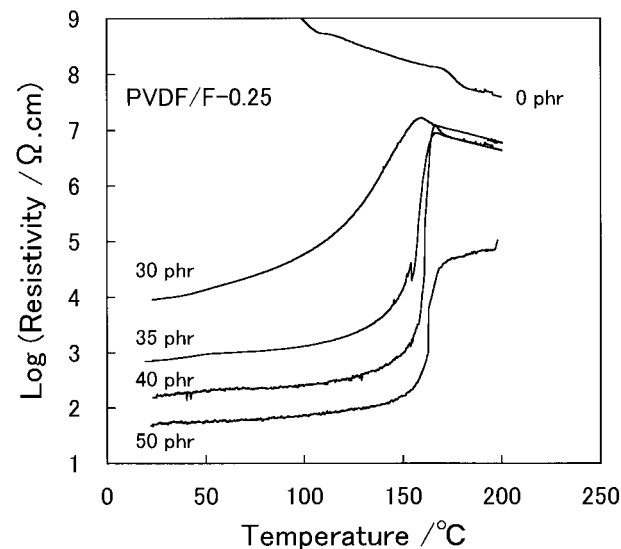
The temperature dependence of the resistivity with different filler concentrations for PVDF/F-0 and PVDF/F-0.25 is illustrated in Figure 5(a,b), respectively. Both mixtures have a significant positive temperature coefficient (PTC) resistance effect near 168°C. The large PTC anomaly is typical for a carbon black-filled semicrystalline polymer (such as polyethylene and PVDF) composites¹⁴⁻¹⁶ and has been attributed to the thermal damage of conductive pathways due to the melting of crystalline. Usually, a strong negative temperature coefficient (NTC) resistance effect can be observed at temperatures above the PTC transition, as shown in Figure 5(a) for PVDF/F-0. This

is ascribed to the high mobility of the carbon particle in the molten matrix and, hence, the reconstruction of conductive networks.^{17,18} A conventional technique to eliminate the NTC effect is crosslinking through either chemical or radiation treatments.¹⁴

However, we find that the NTC effect can also be alleviated or eliminated by fluorination of carbon black. As shown in Figure 6, increase of the fluorine content results in a decrease in the NTC effect. A slight NTC effect for PVDF/F-0.25 should result from the electrical characteristic of pure



(a)



(b)

Figure 5 Temperature dependence of resistivity with different filler concentrations for (a) PVDF/F-0 and (b) PVDF/F-0.25.

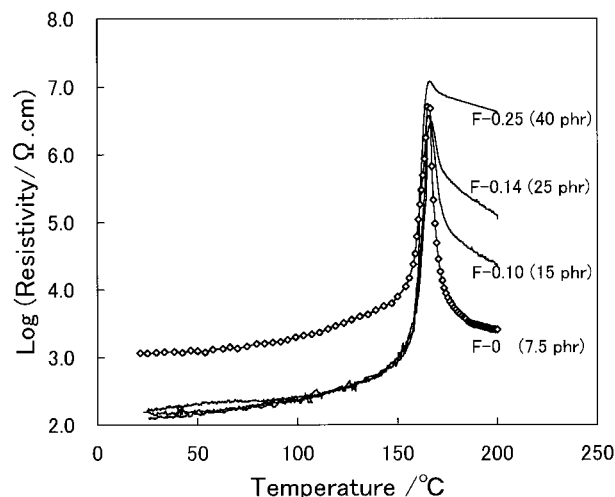


Figure 6 Influence of fluorine content on the NTC effect for PVDF/FCB composites.

PVDF [see the temperature dependence of resistivity curve for pure PVDF in Fig. 5(b)].

Two reasons might be proposed to explain the phenomena: One is that F-0.25 particles have less activity to rebuild the networks due to low self-interactions. However, we noticed that resistivity for all the investigated samples could recover near to their initial value if the temperature is decreased. Another reason is that F-0.25 particles have less mobility due to the strong interactions with the PVDF matrix, just like crosslinking making the polymer have less mobility.

To clarify whether the reduction of the NTC effect arises from F—F interactions between FCB and PVDF or not, LDPE (Petrosen 175, from Toso Co.) was used instead of PVDF so that the matrix has no C—F bonds. The samples of filled 60 and 70 phr F-0.25 were prepared at 150°C for 15 min (both for mixing and pressing). Figure 7 shows the temperature dependence of the resistivity for LDPE/F-0.25 with a comparison of PVDF/F-0.25 (40 phr). It is observed that, for the first run, both the LDPE/F-0.25 samples show a strong NTC effect until the resistivity is decreased to about $10^7 \Omega \text{ cm}$, a value which is at the same level as that of the PVDF/F-0.25 composites. During the second run, the resistivity of both samples only increases to about $10^7 \Omega \text{ cm}$ and then is maintained at that level up to 250°C. The NTC effect is thus eliminated in the LDPE/F-0.25 composites.

It is unclear why all the composites keep the resistivity at about $10^7 \Omega \text{ cm}$ at high temperatures. A possible explanation is that the fluorine

initially bonding with carbon black is reactive at temperatures higher than 170°C, and it can react with LDPE chains, producing a fluorinated polymer at the FCB particle interfaces. Actually, Hamed et al.³ found that fluoroblack can itself cause crosslinking of styrene–butadiene rubber. He suggested that the fluoroblack can react with some ingredient of the rubber, causing the release of hydrogen fluoride, which crosslinks the rubber. Further work is needed to explore this and other possibilities.

Dielectric Behavior

Figure 8 shows the effect of filler concentrations on the dielectric permittivity, ϵ' , and dielectric loss, ϵ'' , for various PVDF/FCB composites. The measurements were performed at room temperature (about 25°C) with a frequency of 8 MHz. As shown in Figure 8(a), ϵ' increases slightly, up to a point a little lower than the percolation concentration obtained from the resistivity–concentration curves (see Fig. 4). Above this point, ϵ' increases at a much faster rate. With increasing the fluorine content, the critical point shifts to a high concentration and the increased rate of ϵ' becomes gradual. Obviously, the dielectric behavior corresponds to the percolation behavior. The same tendency is observed in the filler concentration dependence of ϵ'' as shown in Figure 8(b). A double logarithmic plot of ϵ'' against ϵ' for various PVDF/FCB composites with different filler concentration is given in Figure 9. From the figure,

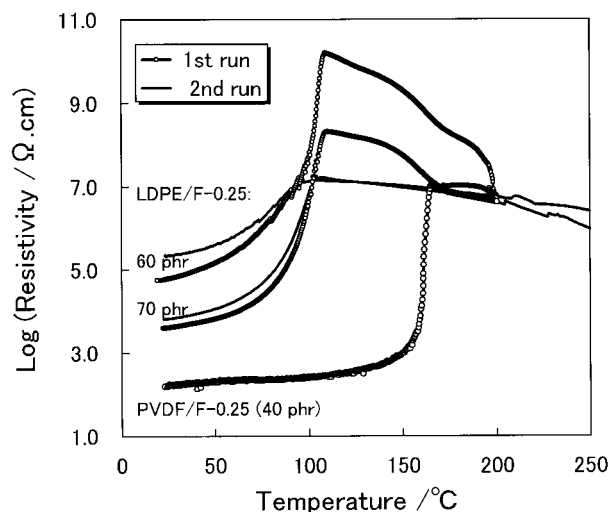
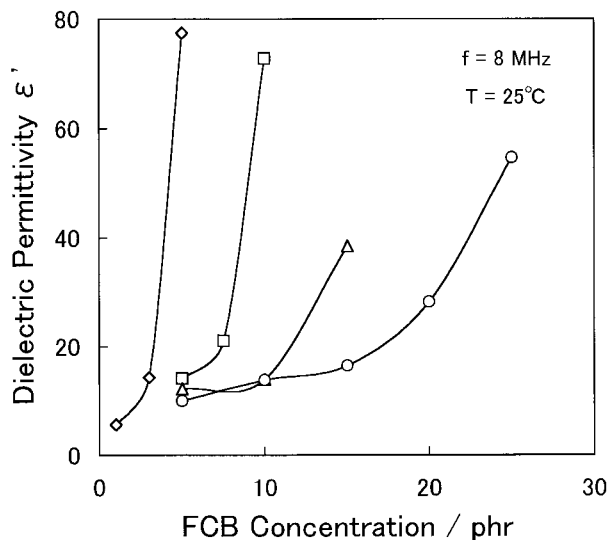
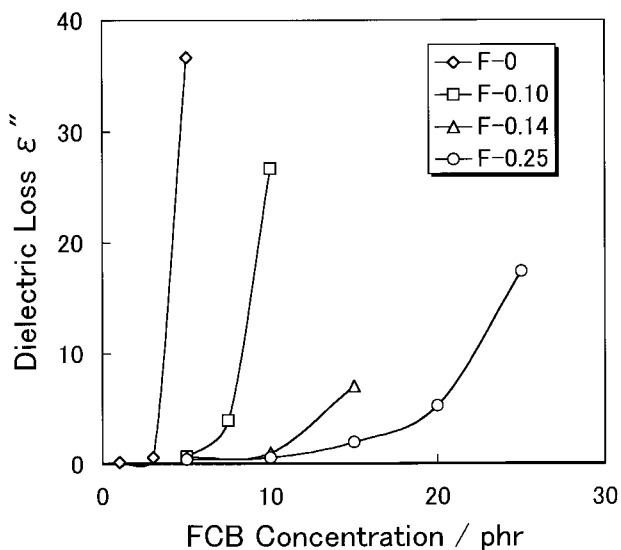


Figure 7 Temperature dependence of resistivity for LDPE/F-0.25 composites in comparison with that of PVDF/F-0.25 composites.



(a)



(b)

Figure 8 Dielectric behavior of various PVDF/FCB composites: (a) dielectric permittivity versus FCB concentration; (b) dielectric loss versus FCB concentration.

we find that all the obtained data are located on one curve, regardless the fluorine content of the FCB used.

Figure 10 shows the frequency dependence of the dissipation factor ($\tan \delta$) for various systems. The filler concentration was selected at the percolation range, where the conductive networks start to form, so as to check the dielectric dissipation behavior of the FCB networks. As shown, the dissipation peak at 1.5 MHz should arise from dipolar relaxation of PVDF segments within the

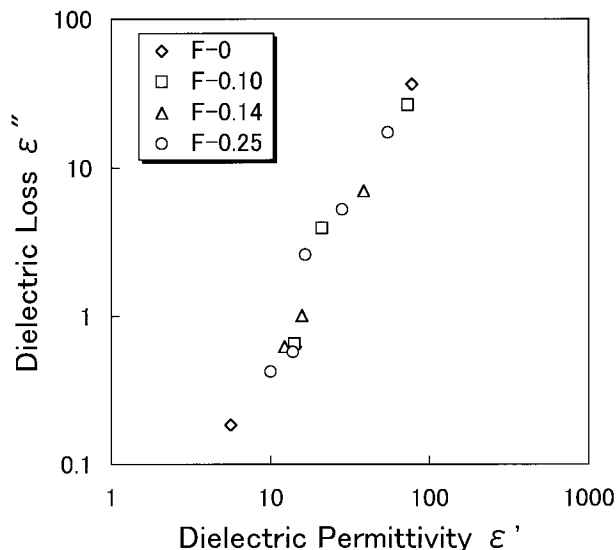


Figure 9 Double logarithmic plot of dielectric permittivity and dielectric loss.

amorphous phase.¹⁹ The broad loss at frequencies lower than 1 kHz is usually ascribed to the interfacial polarization or the Maxwell–Wager–Sillars relaxation²⁰ and, if any, the dc conduction. For F-0.10-filled composites, the third relaxation peak around 10 kHz is found. This may be correlated to the ionic nature of the F–C bond at low fluorine content.⁴

According to Figure 10, a frequency of 8 MHz is too fast for interfacial polarization to arise and there is no contribution of an interfacial effect to

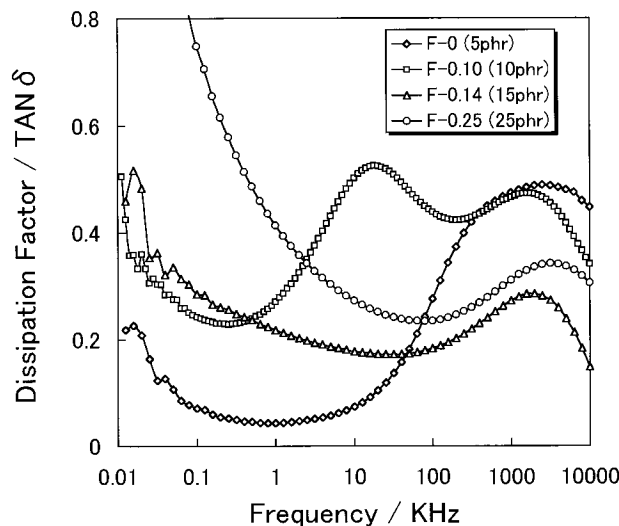


Figure 10 Frequency dependence of dissipation factor ($\tan \delta$) for different PVDF/FCB systems.

ϵ' and ϵ'' . It is also too fast for the dipolar relaxation of the F—C bond on carbon surfaces. This may be the reason why the relation between $\log \epsilon''$ and $\log \epsilon'$ in Figure 8(b) is irrespective of the fluorine content.

CONCLUSIONS

The following is a summarization of the results presented on the development of fluorinated carbon black-filled conductive polymer composite materials:

1. With increasing the fluorine content, the FCB particles prefer to stick together and to form large aggregates rather than particle-contacting chains.
2. Percolation becomes gradual and the percolation concentration shifts to a high concentration with increasing fluorine content.
3. The fluorinated carbon black has a higher PTC intensity than the pristine one in PVDF/FCB composites. Furthermore, the NTC effect can be alleviated or eliminated through increase of the fluorine content both for PVDF/FCB and LDPE/FCB systems.
4. Both the dielectric permittivity and the dielectric loss increase with the FCB concentration. However, the relation between $\log \epsilon''$ and $\log \epsilon'$ at high frequency is independent of the fluorine content.

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