

Dynamic Percolation Phenomenon of Poly(methyl methacrylate)/Surface Fluorinated Carbon Black Composite

A. Katada,¹ Y. Konishi,¹ T. Isogai,² Y. Tominaga,¹ S. Asai,¹ M. Sumita¹

¹Department of Chemistry and Materials Science, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-Ku, Tokyo 152-8552, Japan

²Daikin Industries, Ltd., 1-1 Nishi-Ichitsuya, Settsu-shi, Osaka 566-8585, Japan

Received 15 July 2002; accepted 22 October 2002

ABSTRACT: The electrical resistivity of polymer filled with conductive filler, such as carbon black (CB) particles, is greatly decreased by incorporating the conductive filler. This is called the percolation phenomenon and the critical CB concentration is called the percolation threshold concentration (Φ^*). For CB particle-filled insulating polymer composite at lower than Φ^* , the conductive CB network is constructed in the polymer matrix when the composite is maintained at a temperature higher than the glass-transition temperature or the melting temperature of the polymer matrix. This phenomenon is called dynamic percolation and the time to reach the substantial decrease in resistivity is called percolation time (t_p). To investigate the relationship between the dynamic percolation process and the surface state of CB particles, we used three kinds of carbon black particles such as original carbon black (CB0) and fluorinated carbon black

(FCB010 and FCB025)-filled poly(methyl methacrylate) (PMMA). It was observed that the dynamic percolation curves for CB0-filled PMMA and FCB-filled PMMA composites shifted to a shorter percolation time with increases in both the annealing temperature and the filler concentration. However, the dynamic percolation curves of FCB-filled PMMA showed a gradually decreasing trend compared to that of CB0-filled PMMA composites. The activation energy calculated from an Arrhenius plot of the t_p against the inverse of the annealing temperature was decreased by surface fluorine treatment. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1151–1155, 2003

Key words: fluorinated carbon black; dynamic percolation; poly(methyl methacrylate); conductive polymer composites; electrical resistivity

INTRODUCTION

The physical properties of composites consisting of polymer and carbon black (CB) particles greatly depend not only on the volume fraction of the CB particle but also on their surface state.^{1–11} For example, the dispersion state of surface-treated CB particles in the matrix consisting of immiscible polymer blends was found to be affected by the interfacial free energy calculated from surface energies of the polymer matrix and CB particles.^{1–4} Moreover, the bound rubber thickness estimated from ¹H-NMR analysis of natural rubber (NR)/surface oxidized CB particle composites is lower than that of NR/untreated CB composites.^{5,6} In the matter of surface fluorination, surface fluorine treatment of particles causes the decrease of surface energy.^{7–9}

About the physics of poly(vinylidene fluoride) (PVDF) or low-density polyethylene (LDPE) and surface-fluorinated carbon black (FCB) composite, the percolation curve gradually decreases upon surface fluorine treatment.^{10,11} In addition, the mixing torque

of the composite consisting of styrene-butadiene rubber (SBR) and fluorinated graphite decreased with increasing surface fluorine content, attributed to the weak interaction by surface fluorine treatment.⁷ In this way, FCB particles are expected to constitute a new class of reinforcing or conducting filler.

Furthermore, the electrical resistivity of polymer/conductive filler, such as CB particles, is greatly decreased by incorporating the conductive filler. This phenomenon is called the percolation phenomenon and the critical CB concentration is called the percolation threshold concentration (Φ^*). It was previously reported that the Φ^* is greatly influenced by the melt viscosity of the polymer matrix and the molding time.^{12–14} Those results indicate that CB particles in a polymer matrix actually require time to move in forming the conductive network. On the other hand, the dynamic percolation measurement is the investigation by tracing in real time the time dependency of electrical resistivity during annealing treatments under the molten temperature of the polymer matrix.^{15–17} The percolation time (t_p) is characterized at a certain annealing time when the electrical resistivity starts to decrease drastically. This dynamic percolation measurement is an effective tool to determine the growth of the construction of a CB conductive network in the polymer matrix.

Correspondence to: M. Sumita (msumita@o.cc.titech.ac.jp).

TABLE I
Characteristics of Fluorinated Carbon Black Particles

Sample	F/C atomic ratio	Diameter (nm)	Surface area ^a (m ² /g)	Surface energy ^a γ^d (mJ/m ²)
CB0	0.0	42	47.9	126
FCB010	0.10	42	57.0	121
FCB025	0.25	42	68.1	99

^a Measured by inverse gas chromatography (IGC); probe; *n*-octane (C₈); column temperature; 110°C.

The objective of this work was to clarify the relationship between the dynamic percolation phenomenon and the surface state of filler particles, prepared by original CB particle- or FCB particle-filled PMMA. Two problems were considered: (1) the effect of using the FCB on the construction of the conductive network under the dynamic percolation process and (2) the thermodynamical consideration, which is the effect of decreasing the surface energy by surface fluorination treatment on the dynamic percolation.

EXPERIMENTAL

Sample preparation

Poly (methyl methacrylate) (PMMA, VH; Mitsubishi Rayon Co., Japan) was used as a polymer matrix. The weight-average molecular weight (M_w) and the number-average molecular weight (M_n) were 100,000 and 70,000 g/mol, respectively. Those data were obtained from Mitsubishi Rayon Corporation. The glass-transition temperature (T_g) of PMMA was determined by differential scanning calorimetry (DSC) under a heating rate of 20°C/min and was found to be 130°C.

Three kinds of carbon black particles (CB0, FCB010, and FCB025) with different F/C atomic ratios of 0, 0.10, and 0.25 (supplied by Daikin Industries Co.) were used as conductive fillers. The FCB particles were synthesized by the direct fluorination of CB0 at about 400°C.^{18,19} The physical characteristics of the fillers are summarized in Table I. As shown in Table I, the diameters of various FCB particles did not change with increasing F/C atomic ratio. Meanwhile, the Brunauer–Emmett–Teller (BET)²⁰ surface area increased concomitantly with the increase in the F/C atomic ratio. On the other hand, the surface energy dispersive component (γ^d) decreased with the increase in the F/C atomic ratio.

In this work, the CB0, FCB010, and FCB025 particles and PMMA matrix were dried at 110°C for 24 h under vacuum before mixing. The mixing process was performed using a two-roll mill for 20 min at 190°C. The freestanding sheets (thickness of 1.0 mm) were obtained from the mixtures using compression molding at 190°C for 1 min under a pressure of 19.6 MPa, followed by quenching in cold water.

Measurements

The electrical resistivity was measured by use of a Keithley 487 picoammeter (Keithley Metrabyte, Taunton, MA) equipped with a dc voltage source at a given annealing temperature. The specimen (width \times length, 20 \times 20 mm²) was cut from the center area of the molded freestanding sheet and was fixed on a glass slide using polyimide tape. Silver paste was used to ensure good contact between the sample surface and copper electrodes. The sample was then placed in a temperature-controlled chamber. Nitrogen gas was introduced during the measurement to prevent oxidation of the samples. The applied voltage for the measurement was 1 V and the time interval was 10 s.

RESULTS AND DISCUSSION

For conductive polymer composite materials, the electrical resistivity at room temperature is one of the important properties. Figure 1 shows the CB volume fraction (V_f) dependency of the room-temperature resistivity for original carbon black (CB0) and surface-fluorinated carbon blacks (FCB010, FCB025) filled PMMA. The percolation (i.e., the substantial decrease in resistivity by forming a conductive CB network in an insulating polymer matrix) takes place for all of the

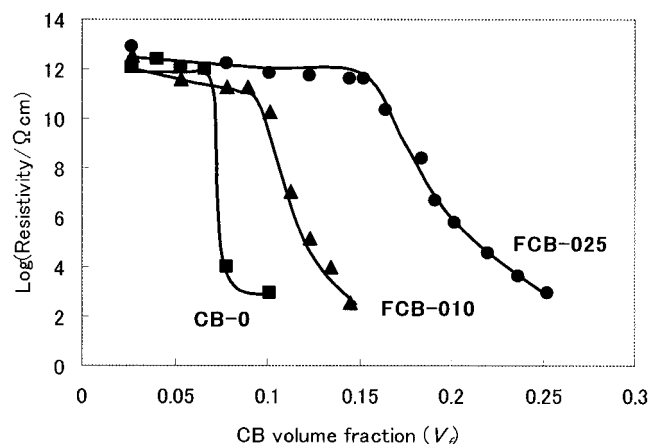


Figure 1 CB volume fraction dependency of the room-temperature resistivity for PMMA filled with CB0, FCB010, and FCB025 composites.

CB0- and FCB-filled PMMA composites. The critical CB concentration is called the percolation threshold (Φ^*). It was found that the Φ^* of PMMA filled with CB0 composite was about 0.06; with FCB010, about 0.10; and with FCB025, about 0.16. Additionally, it was found that the percolation curves decreased gradually as a result of the increase in surface fluorine content. This tendency is similar to that of PVDF¹⁰ and LDPE¹¹ filled with FCB composites.

In CB-filled polymer composites, CB particles move to coalesce, through Brownian motion at molten temperatures higher than the T_g or the melting temperature (T_m) of the polymer matrix, and finally form continuous conductive networks. Consequently, the resistivity of polymer composite is substantially decreased. By means of isothermal treatments, this process can be traced in real time by *in situ* recording of the variation of electrical resistivity with the annealing time. Figure 2(a)–(c) show the time dependency of resistivity at 180°C for CB0-, FCB010-, and FCB025-filled PMMA composites that have various CB concentrations. Those CB concentrations are lower than the Φ^* (see Fig. 1). In Figure 2 the decrease of resistivity is observed to result from the rearrangement of conductive CB particles in the PMMA matrix.

When the annealing time increased, slightly at first and then rapidly when a critical time was reached, the beginning stages of the transition from an insulator to a conductor occurred. This critical time is defined as the percolation time (t_p) and this phenomenon is called dynamic percolation.^{15,16} With increasing the CB content, given that the conductive CB network is constructed with a slight migration of the dispersed CB particles, the dynamic percolation curves shifted to a shorter percolation time. From Figure 2, the percolation curves of FCB010- and FCB025-filled PMMA composites showed gradually decreasing trends compared with that of CB0-filled PMMA composite, in the same manner as that of the as relationship between resistivity and CB content (see Fig. 1). For the conductive CB particle-filled insulating polymer, the electrical conduction mechanism of the percolation region contributes to the tunneling-conduction mechanism.^{21–25} In particular, the resistivity related to tunneling conduction is exponentially decreased with decreasing the CB interparticle distance in a conductive CB network.^{26,27} In the case of surface-fluorinated CB-filled PMMA composites, the CB interparticle distance in a conductive CB network is widened by the surface-treated fluorine layer. Accordingly, the percolation curves of fluorinated carbon black-filled PMMA composites show a gradually decreasing trend compared with that of the original carbon black-filled PMMA.

Figure 3(a) and (b) show the annealing time dependency of the resistivity for CB0-filled PMMA composites at various temperatures. With increasing annealing temperature, the dynamic percolation curves

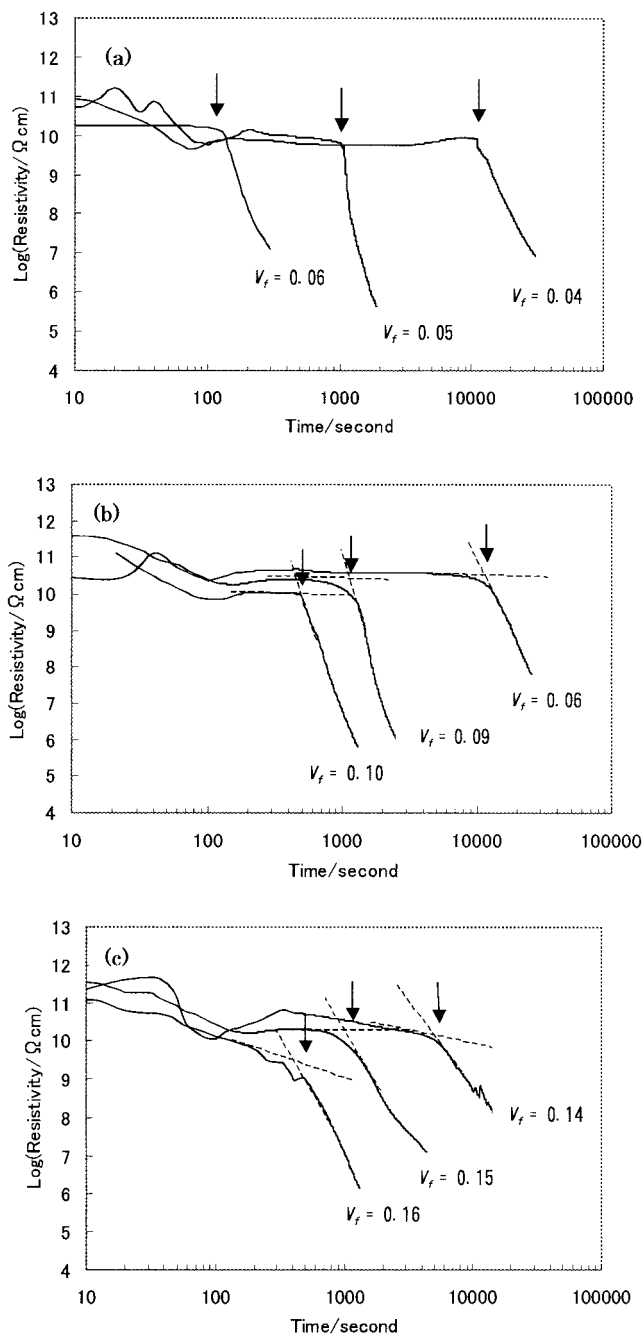


Figure 2 Dynamic percolation curves of (a) PMMA/CB0, (b) PMMA/FCB010, and (c) PMMA/FCB025 composites with various CB volume fractions at 180°C.

shifted to a shorter percolation time. Moreover, the shapes of the dynamic percolation curves did not change with the annealing temperature. The data of annealing time dependency of the resistivity for FCB010- and FCB025-filled PMMA composites are not presented here.

Figure 4 shows the Arrhenius plots of the t_p versus the inverse of annealing temperature for CB0, FCB010, and FCB025 composites, the CB volume fractions of which are 0.06; 0.10, and 0.16, respectively. A linear

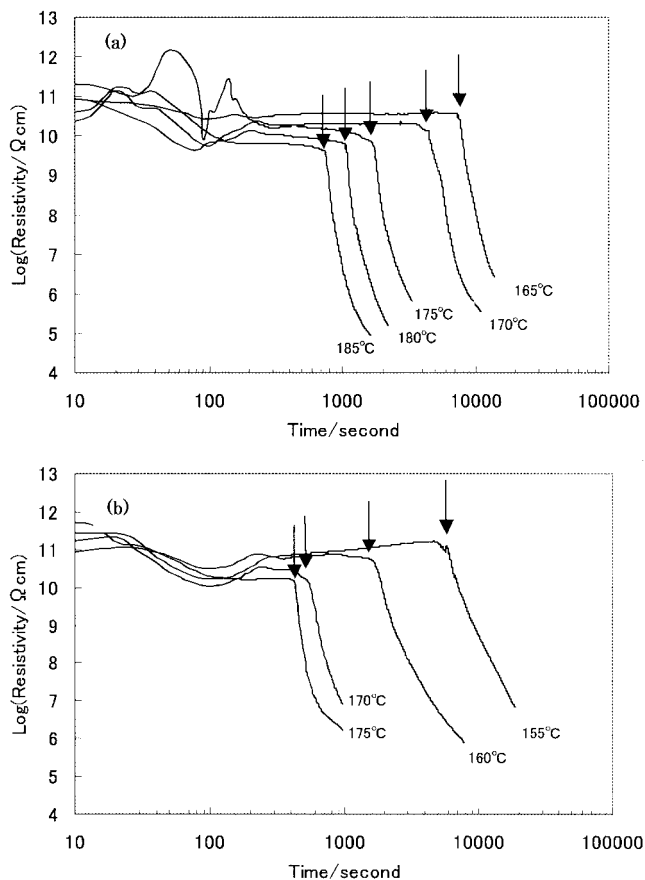


Figure 3 Dynamic percolation curves for PMMA/CB0 for (a) $V_f = 0.05$ and (b) $V_f = 0.06$ at various temperatures.

relationship for various concentrations was found. From these plots we calculated the activation energy using the equation, $\ln(1/t_p) = \ln A - E_a/RT$, where E_a is the activation energy, R is the gas constant, and T is the absolute temperature. The E_a value calculated from dynamic percolation is not dependent on CB content, as previously suggested.^{15,16} The contact process between CB particles can be equivalent to the excluding process of polymer molecules between CB particles, and thus, the mobility of CB particles actually reflects the mobility of the polymer layer between CB particles. Because the particle-particle interaction force of CB is very weak, the shear stress and shear rate in the polymer melts are so weak that the movement of the polymer layer between CB particles might be regarded as the state of zero shear rate. Accordingly, the E_a calculated from a zero shear-rate viscosity of the neat polymer matrix and the E_a calculated from dynamic percolation have almost identical values.¹⁵ In this study, we examined the relationship between E_a values calculated from dynamic percolation and the surface energies of filler particles. From Figure 4, one sees that the E_a decreased by surface treatment with fluorine. Compared to the PMMA/oxidized carbon black composites in our previous study,¹⁵ this ten-

dency, the decreasing E_a with surface treatment of CB, is opposite to that for the composite with oxidized carbon blacks. The decrease of the E_a with the fluorine content can be understood on the basis of the following thermodynamic considerations.

Generally, incorporation of CB particles into the polymer matrix will inevitably increase the system energy because of their incompatibility. In our case, surface modification by fluorine caused the decrease in the dispersive component of surface energy (γ^d). The decrease of γ^d is accounted for by the "pollution" with treated functional groups of the adsorption sites.^{28,29} The fluorine on the treated CB surface is considered a nonadsorption site to organic molecules. Therefore, the fluorine-treated CB particles easily aggregate under applied temperature as a result of the weakened interaction between the FCB particles and the PMMA matrix. This tendency, the weakening interaction between filler particles and the polymer matrix attributed to the decreasing surface energy of CB particles, is similar to the relationship between general rubbers [natural rubber (NR), styrene-butadiene rubber (SBR), and acrylonitrile-butadiene rubber (NBR)] and alkylated silica.^{30,31}

CONCLUSIONS

In summary, results on the characteristics of surface-fluorinated carbon black-filled PMMA composite materials are presented. In particular we examined the dynamic process of forming conductive networks in FCB-filled PMMA composites by tracing in real time the time dependency of electrical resistivity during isothermal treatments.

The percolation curves for FCB-filled PMMA showed a gradually decreasing trend with increasing surface fluorine content.

The dynamic percolation curves for the CB0-, FCB010-, and FCB025-filled PMMA composites

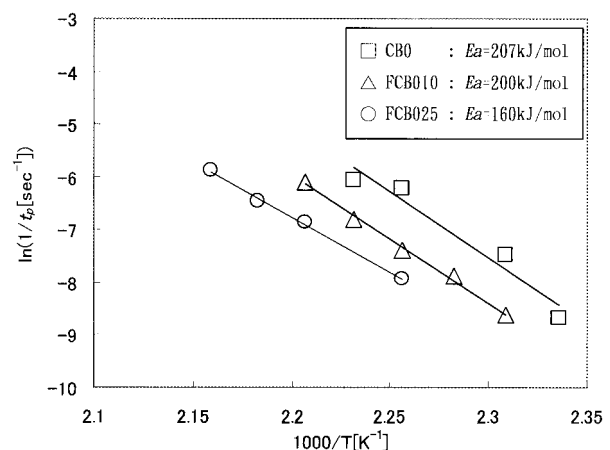


Figure 4 Arrhenius plots of the percolation time (t_p) for PMMA/CB0 and PMMA/FCB composites.

shifted to a shorter percolation time with an increase of both the annealing temperature and the filler concentration. The dynamic percolation curves of FCB-filled PMMA showed a gradually decreasing trend compared to that of the CB0-filled PMMA. This tendency was similar to the percolation curves of the CB content versus resistivity for FCB-filled PMMA composites. The activation energy (E_a) was also calculated from an Arrhenius plot of the t_p inverse of the annealing temperature. As an experimental result, the decreased E_a of surface fluorinated CB indicates the weak interaction between PMMA and the FCB particles.

References

1. Sumita, M.; Sakata, K.; Asai, S.; Miyasaka, K.; Nakagawa, H. *Polym Bull* 1991, 25, 265.
2. Asai, S.; Sakata, K.; Sumita, M.; Miyasaka, K. *Polym J* 1992, 24, 415.
3. Mamunya, Y. P. *J Macromol Sci Phys* 1999, B38, 615.
4. Wu, S.; Asai, S.; Sumita, M. *Sen-i-Gakkaishi* 1993, 49, 103.
5. Asai, S.; Kaneki, H.; Sumita, M.; Miyasaka, K. *J Appl Polym Sci* 1991, 43, 1253.
6. Serizawa, H.; Nakamura, T.; Ito, M.; Tanaka, K.; Nomura, A. *Polym J* 1983, 3, 201.
7. Rodriguez, J.; Hamed, G. R. *Rubber Chem Technol* 1996, 69, 286.
8. Nakahara, M.; Ozawa, K.; Sanada, Y. *J Mater Sci* 1994, 29, 1614.
9. Setoyama, N.; Li, G.; Kaneko, K. *Adsorption* 1996, 2, 293.
10. Wu, G.; Zhang, C.; Miura, T.; Asai, S.; Sumita, M. *J Appl Polym Sci* 2000, 80, 1063.
11. Katada, A. M. S. Thesis, Tokyo Institute of Technology, Japan, 2000.
12. Sumita, M.; Abe, H.; Kayaki, H.; Miyasaka, K. *J Macromol Sci Phys* 1986, B25, 171.
13. Asai, S.; Sumita, M. *J Macromol Sci Phys* 1995, B34, 283.
14. Zhang, C.; Yi, X.-S.; Asai, S.; Sumita, M. *Compos Interfaces* 1999, 6, 218.
15. Wu, G.; Asai, S.; Zhang, C.; Miura, T.; Sumita, M. *J Appl Phys* 2000, 88, 1480.
16. Wu, G.; Asai, S.; Sumita, M. *Macromolecules* 2002, 35, 1708.
17. Wu, G.; Asai, S.; Sumita, M. *Polymer* 2001, 42, 3271.
18. Isogai, T.; Maruyama, S.; Yamana, M.; Kubo, M. In: *Proceedings of the 21st Annual Meeting of the Carbon Society, Japan, 1994*; Abstr. 278.
19. Isogai, T.; Kawashima, T.; Uehara, H.; Maruyama, S.; Yamaguchi, F.; Kubo, M.; Hattori, Y.; Touhara, H. In: *Proceedings of the International Symposium on Carbon, 1998*; Abstr. 24.
20. Brunauer, S.; Emmet, P. H.; Teller, J. *J Am Chem Soc* 1938, 60, 309.
21. Sichel, E. K.; Gittleman, J. T. *J Electron Mater* 1982, 11, 699.
22. Chung, K. T.; Sabo, A.; Pica, A. P. *J Appl Phys* 1982, 53, 10.
23. Sichel, E. K. *Carbon Black Polymer Composites*; Marcel Dekker: New York, 1982.
24. Ezquerro, T. A.; Kulesca, M.; Balta-Calleja, F. J. *Synth Met* 1991, 41, 915.
25. Balberg, I. *Phys Rev Lett* 1987, 21, 1305.
26. Bloom, I.; Balberg, I. *Phys Rev B* 1999, 59, 12196.
27. Balberg, I. *Carbon* 2002, 40, 139.
28. Papirer, E.; Lacrox, R.; Donnet, J. B. *Carbon* 1996, 34, 1521.
29. Papirer, E.; Li, S.; Balard, H.; Jagiello, J. *Carbon* 1991, 8, 1135.
30. Ou, Y. C.; Yu, Z. Z.; Vidal, A.; Donnet, J. B. *Rubber Chem Technol* 1994, 67, 834.
31. Ou, Y. C.; Yu, Z. Z.; Vidal, A.; Donnet, J. B. *J Appl Polym Sci* 1996, 59, 1321.