Colloid Polym Sci (2005) 283: 367–374
DOI 10.1007/s00396-004-1149-5

ORIGINAL CONTRIBUTION

Arinobu Katada
Yose Fachmi Buys
Yoichi Tominaga
Shigeo Asai
Masao Sumita

Resistivity control in the semiconductive region for carbon-black-filled polymer composites

Received: 10 December 2003
Accepted: 1 April 2004

A. Katada · Y. F. Buys · Y. Tominaga
S. Asai · M. Sumita (✉)
Department of Chemistry and Materials Science, Tokyo Institute of Technology,
2-12-1 Ookayama, Meguro-Ku,
152-8552 Tokyo, Japan
E-mail: msumita@o.cc.titech.ac.jp

Abstract It is known that the electrical volume resistivity of insulating polymers filled with conductive fillers, such as metal particles and/or carbon black (CB) particles, suddenly decreases at a certain content of the filler. Therefore, it is very difficult to control the resistivity in the semiconductive region for the CB-filled composites. We examined two effects to control the electrical volume resistivity in the semiconductive region for CB-filled polymer composites. One is the effect of fluorination of the CB surface on the percolation behavior using surface-fluorinated CB particles as a filler. The other is the effect of copolymerization of polyethylene (PE) with a vinyl acetate (VA) functional group on the percolation behavior using poly(ethylene-*co*-VA) (EVA) as a matrix. By immersion heat measurements, it was found that the London dispersive component turned out to be the predominant factor of the surface energy of fluorinated CBs. The London dispersive component of the surface energy significantly decreased, while the polar component slightly increased on increasing the fluorine content. The resistivity of fluorinated a CB-filled low-density PE composite showed that the percolation threshold increased, and the transition from the insulating state to the conductive state became sluggish, on increasing the fluorine content. In the case of using EVA as a matrix, on the other hand, the percolation curve was moderated with the increase in the VA content. Therefore, copolymerization of PE with VA is also suitable for the design of a semiconductive polymer composite as well as for fluorination of the CB surface. The total surface area per unit mass of dispersed CB particles in the EVA matrix estimated from small-angle X-ray scattering decreased with increasing CB content. Further, the decrease in the surface area is moderated with an increase in VA content. It was found that the difference in the percolation curve is due to the difference in the dispersive state of CB particles.

Keywords Electrical resistivity · Percolation · Surface energy · Small-angle X-ray scattering · Poly(ethylene-*co*-vinyl acetate)

Introduction

It is known that the electrical volume resistivity of insulating polymers filled with conductive fillers, such as metal and/or carbon black (CB), discontinuously decreases at a certain content of the filler. This sharp break in the relation between the content of conductive particles and the resistivity of composites implies some sudden change in the dispersing state of the conductive particles, i.e., the aggregation of the particles to form networks which facilitate the electrical conduction through the composite. This transition phenomenon is called the percolation phenomenon, and this critical CB volume fraction is called the percolation threshold (V_f*). The transition-like change in the resistivity of these composites has prompted much research and many researchers have proposed models regarding the transition-like behavior [1, 2, 3, 4, 5, 6]. Buche [1, 2] tried to explain the S-shaped resistivity curves of binary mixtures using the concept of polymer gelation, as proposed by Flory. Miyasaka and coworkers [3, 4] proposed the thermodynamic percolation model which emphasizes the importance of the interfacial interaction between CB particles and the polymer matrix. Additionally, Wessling [5] also proposed a model on the basis of thermodynamics. Especially, the interfacial energy between a CB particle and the polymer matrix is the most important role in determining V_f* in these thermodynamic models, because these models assume that the interfacial energy acts as a driving force for aggregation of CB particles in the polymer matrix. Therefore, the surface energy measurement of CB particles is necessary for determining V_f*. At the same time, the control of volume resistivity in the semiconductive region, which ranges from 10^5 to 10^8 Ω cm, for the CB-filled polymer composite is also a very important subject from an industrial point of view. Therefore, many authors have reported research regarding the resistivity control in the semiconductive region for CB-filled polymer composite systems [7, 8, 9, 10, 11].

On the other hand, fluorinated CB particles have been fabricated to be a new class of reinforcing and conductive filler [8, 9, 10, 11, 12, 13]. Causing CB to react with elemental fluorine, we can adjust both the surface energy and the electrical conductivity of the CB particle. This is caused by the forming of strong carbon–fluorine covalent bonds at the surfaces [14, 15]. For this reason, we can expect that the use of fluorinated CB particles as a filler is effective for controlling resistivity in the semiconductive region for a CB-filled polymer composite. Additionally, poly(ethylene-*co*-vinyl acetate) (EVA) has also been found to be a suitable matrix for CB-filled polymer composites because the polarity and the surface energy of EVA can be changed by variation in the vinyl acetate (VA) content [4, 16, 17, 18, 19]. In particular, it has been reported that the percolation curve becomes moderate with increasing VA content [4]. That is to say, the use of EVA as a polymer matrix is also suitable for the design of semiconductive polymer composites. However, the effect of the VA content on the dispersion state of CB particles by means of quantitative analysis has not been reported. On the other hand, small-angle X-ray scattering (SAXS) measurement is known to be an effective tool for the quantitative analysis of the dispersion state of filler particles [20, 21, 22, 23]. The main requirement is that there is sufficient electron density difference between the different phases such that appreciable scattering of X-rays occurs.

The objective of this work is to clarify the effect of the CB surface state on the percolation behavior using fluorinated CB particles as a filler. Moreover, we demonstrated that the effect of copolymerization of polyethylene (PE) with a VA functional group on the dispersion state of CB particles by means of SAXS measurement. Further, the relationship between the percolation curve and the total surface area per unit mass of CB particles in an EVA matrix calculated from the SAXS profile was examined.

Experimental

CB particles used

Three kinds of conductive CB particles with different F-to-C atomic ratios of 0, 0.10 and 0.25, i.e., CB0, FCB010 and FCB025, supplied from Daikin Industries Co. Japan, were used. The F-to-C atomic ratio was estimated using elemental analysis as described elsewhere [14, 15]. The FCB010 and FCB025 particles were synthesized by direct fluorination of acetylene black at 400 °C. By the fluorination, the C–F covalent bond in the sp^3 hybrid orbital is formed; thus, the π-electron density in some part of the surface is diminished. The particle diameter and the density of these particles are 42 nm and 1.95 g/cm^3, respectively. We observed that the particle diameter is not changed by fluorine treatment from scanning electron microscopy (SEM) photographs [9].

Immersion heat measurements of CB particles

The FCB particles were evacuated at 200 °C for 24 h prior to measurement. For the calorimetric determination of the immersion heat, the FCB particles were sealed in a glass ampoule after evacuation. Formamide (Kanto chemical Co., purity above 98%) and *n*-octane (Kanto Chemical Co., Pure) were the liquids employed for immersion heat measurements. Formamide is bipolar, while *n*-octane is apolar. The immersion heats were measured using a twin-conduction-type microcalorimeter (Tokyo RIKO Co., Japan). The measurements were performed at room temperature of 25 °C. The ampoules were broken simultaneously in each liquid, so that the CB particles were immersed into the solvent, and the immersion heat flow from cells versus time was recorded.

Preparation of the CB-filled polymer composite film

The CB0, FCB010 and FCB025 particles were dried at 110 °C under vacuum before mixing. The CB particles and the polymer were mixed together using a two-roll mill (Nishimura machinery Co.) at about 120 °C. The freestanding sheets with a thickness of about 1.0 mm were obtained from the mixtures by a compression-molding method at 120 °C for 3 min under a pressure of 19.6 MPa using a hot press (Technosupply Co. Japan), followed by quenching in cold water.

Electrical volume resistivity measurement of CB-filled polymer composite films

The electrical volume resistivity was measured using a Keithley 487 picoammeter (Keithley Instruments) equipped with a direct current (d.c.) voltage source. The specimen (width times length, 20×20 mm^2) was cut from the freestanding sheet and fixed on a glass slide using polyimide tape. Silver paste was used to ensure good contact between the specimen surface and the copper electrodes. The specimens were then placed in a temperature-controlled chamber. The volume resistivity measurements were performed in the thickness direction of the freestanding sheets by using a two-terminal method under d.c. conditions at room temperature of 25 °C.

SEM observation

The dispersion of CB particles in the polymer matrix was observed using a field-emission-type scanning electron microscope (FE-SEM S800, HitachiI High-Technologies Co.). Specimens were fractured in liquid nitrogen. Then, the broken surface was etched by Ar ions for 15 min using an Eiko IB-3 apparatus and was coated with Pt–Pd.

SAXS measurement

SAXS measurements were carried out using a Rigaku RU-200, working at 50 kV and 180 mA, with slit-collimated Cu Kα radiation of wavelength 0.15418 nm. The SAXS intensity was measured in the scattering angle range from 0.10° to 2.5° using a scintillation counter at room temperature. The widths of the first, second, receiving and scattering slits were 0.08, 0.06, 0.1 and 0.25 mm, respectively. The camera length was 360 mm and a Ni filter was put just before the receiving slit.

Results and discussion

Surface energy of CBs estimated from immersion heat measurements

The most popular method for determining the surface energy is based on the contact angle measurement, but in the case of fine materials such as CB particles, it is very difficult to prepare a sample with a proper surface for the measurement. On the other hand, immersion heat measurement, which is the heat measurement method by direct immersion in a liquid with the CB particles, seems to be a more reliable method. Therefore, we estimated the surface energy of CB particles from the immersion heat measurement. In the measurement, *n*-octane and fromamide were used as liquids because their boiling temperatures are much higher than the measurement temperature (25 °C), and their surface tensions, i.e., London dispersive component, polar component and their temperature dependence, have been defined in detail by much research. The measured immersion heats per unit surface area, ΔH_i, are shown in Table 1. The interfacial interaction between the CB surface and the organic liquid is governed mainly by van der Waals interaction because the surface energy of CB is dominated mainly by van der Waals intermolecular interaction. Therefore, almost all molecules of an apolar organic liquid such as *n*-octane interact with the CB surface. Consequently, a higher absolute value was found for *n*-octane, and a lower absolute value was found for formamide.

Immersion heat calorimetry is a powerful technique to determine the surface free energies of finely divided solids. For the immersion of a solid into a liquid, the Gibbs free-energy change is

$$\Delta G_{sl} = \gamma_{sl} - \gamma_s, \tag{1}$$

where γ_{sl} is the solid–liquid interfacial free energy, and γ_s is the free energy of the solid.

The free energy of a solid or a liquid can be written as the sum of a contribution due to London dispersion interactions, γ^d, and polar interactions, γ^p, so that

$$\gamma = \gamma^d + \gamma^p. \tag{2}$$

Using the geometric approach for the London dispersion and polar components, the interfacial free energy between a solid and a liquid can be expressed in the form [25]

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\sqrt{\gamma_s^d \gamma_l^d} - 2\sqrt{\gamma_s^p \gamma_l^p}. \tag{3}$$

Table 1 Specific immersion heat (ΔH_i/ mJ/m^2) of fluorinated carbon blacks in *n*-octane and formamide at 25 °C

	n-Octane	Formamide
CB0	−127	−119
FCB010	−83.5	−78.8
FCB025	−65.6	−63.7

Introducing Eq. (3) into Eq. (1), we obtain

$$\Delta G_{\mathrm{sl}} = \gamma_{\mathrm{l}} - 2\sqrt{\gamma_{\mathrm{s}}^{\mathrm{d}}\gamma_{\mathrm{l}}^{\mathrm{d}}} - 2\sqrt{\gamma_{\mathrm{s}}^{\mathrm{p}}\gamma_{\mathrm{l}}^{\mathrm{p}}}. \tag{4}$$

Therefore, the immersion heat, ΔH_{i}, can be obtained as follows:

$$\begin{aligned}\Delta H_{\mathrm{i}} &= \Delta G_{\mathrm{sl}} - T\frac{\partial \Delta G_{\mathrm{sl}}}{\partial T}\\ &= \gamma_{\mathrm{l}} - 2\sqrt{\gamma_{\mathrm{s}}^{\mathrm{d}}\gamma_{\mathrm{l}}^{\mathrm{d}}} - 2\sqrt{\gamma_{\mathrm{s}}^{\mathrm{p}}\gamma_{\mathrm{l}}^{\mathrm{p}}}\\ &\quad -T\left(\frac{\partial \gamma_{\mathrm{l}}}{\partial T} - 2\sqrt{\gamma_{\mathrm{l}}^{\mathrm{d}}}\frac{\partial\sqrt{\gamma_{\mathrm{s}}^{\mathrm{d}}}}{\partial T} - 2\sqrt{\gamma_{\mathrm{s}}^{\mathrm{d}}}\frac{\partial\sqrt{\gamma_{\mathrm{l}}^{\mathrm{d}}}}{\partial T} - 2\sqrt{\gamma_{\mathrm{l}}^{\mathrm{p}}}\frac{\partial\sqrt{\gamma_{\mathrm{s}}^{\mathrm{p}}}}{\partial T}\right.\\ &\quad \left. - 2\sqrt{\gamma_{\mathrm{s}}^{\mathrm{p}}}\frac{\partial\sqrt{\gamma_{\mathrm{l}}^{\mathrm{p}}}}{\partial T}\right),\end{aligned} \tag{5}$$

where T is the absolute temperature. A value of $\partial\gamma_{\mathrm{s}}^{\mathrm{d}}/\partial T = -0.07$ mJ m^{-2} K^{-1} has been established [26]. Additionally, we assumed that $\partial\gamma_{\mathrm{s}}^{\mathrm{p}}/\partial T = 0$ mJ m^{-2} K^{-1}, since the surface free energy of CB particles is mainly dominated by London dispersive forces [27]. The values of the surface tension of *n*-octane and formamide at 25 °C, $\gamma_{\mathrm{l}}^{\mathrm{d}}$ and $\gamma_{\mathrm{l}}^{\mathrm{p}}$, as well as their temperature coefficients were taken from the literature [28, 29] and are listed in Table 2. Introducing the data of Table 1 and Table 2 into Eq. (5), we obtained the values of $\gamma_{\mathrm{s}}^{\mathrm{d}}$, $\gamma_{\mathrm{s}}^{\mathrm{p}}$ and the total surface energy, γ_{s}, of FCB particles and they are listed in Table 3. As shown in Table 4, it was found that the surface energies of CB0, FCB010 and FCB025 are dominated mainly by London dispersive forces, and $\gamma_{\mathrm{s}}^{\mathrm{d}}$ significantly decreased with increasing fluorine content. The intermolecular interaction by London dispersive forces arises from the interaction of fluctuating electric dipoles with induced dipoles in neighboring atoms or molecules [30]. Therefore, the decrease of γ^{d} by the existence of the fluorine atom is due to weak intermolecular interaction caused by the extreme electronegativity of the fluorine atoms [31]. On the other hand, it was found that $\gamma_{\mathrm{s}}^{\mathrm{p}}$ increased with increasing F-to-C atomic ratio. This result suggests that the fluorination to the CB surface causes intermolecular interaction other than the interaction by van der Waals forces.

Table 2 The surface tension of *n*-octane and formamide (γ/mJ/m^2) at 25 °C, London dispersive component ($\gamma_{\mathrm{l}}^{\mathrm{d}}$), polar component ($\gamma_{\mathrm{l}}^{\mathrm{p}}$) and their temperature dependence [28, 29]

Liquid	γ_{l}	$\gamma_{\mathrm{l}}^{\mathrm{d}}$	$\gamma_{\mathrm{l}}^{\mathrm{p}}$	$\partial\gamma_{\mathrm{l}}/\partial T$	$\partial\gamma_{\mathrm{l}}^{\mathrm{d}}/\partial T$	$\partial\gamma_{\mathrm{l}}^{\mathrm{p}}/\partial T$
n-Octane	21.3	21.3	0	−0.095	−0.095	0
Formamide	57.16	38.34	18.82	−0.168	−0.132	−0.036

Table 3 The values of the percolation threshold (V_{f}*) and the interfacial energy (K/mJ/m^2) for several low-density polyethylene composites

	K	V_{f}*
LDPE/CB0	28.4	0.11
LDPE/FCB010	8.30	0.14
LDPE/FCB025	7.05	0.21

The effect of CB surface fluorination on percolation behavior for CB-filled polymer composite systems

The dependence of the electrical volume resistivity (ρ) on the CB volume fraction (V_{f}) at room-temperature for low-density PE (LDPE, density 0.925 g/cm^3) filled with CB0, FCB010 and FCB025 composite systems is shown in Fig. 1. Percolation (i.e., the substantial decrease in resistivity by forming a CB network in an insulating polymer matrix) takes place for all the samples. The critical CB volume fraction is called the percolation threshold (V_{f}*). V_{f}* is defined as the critical volume fraction when the resistivity decreases suddenly for CB-filled polymer composites [1, 2, 3, 4, 5, 6]. In the case of almost all the CB-filled polymer composites, in general, ρ decreases exponentially for a little increase in V_{f} above V_{f}*. From Fig. 1, it was found that V_{f}* increased with

Table 4 Surface free energy of fluorinated carbon blacks (γ_{s}/mJ/m^2) at 25 °C, London dispersive component ($\gamma_{\mathrm{s}}^{\mathrm{d}}$) and polar component ($\gamma_{\mathrm{s}}^{\mathrm{p}}$), estimated from immersion heat measurements

	F-to-C atomic ratio	$\gamma_{\mathrm{s}}^{\mathrm{d}}$	$\gamma_{\mathrm{s}}^{\mathrm{p}}$	γ_{s}
CB0	0	119	0.77	120
FCB010	0.10	62.0	3.97	66.0
FCB025	0.25	42.8	6.60	49.4

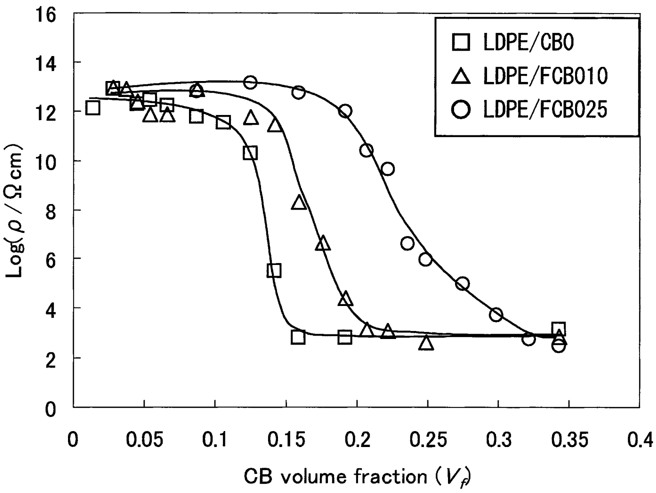

Fig. 1 Relationships between the volume resistivity (ρ) and the carbon black (*CB*) volume fraction (V_{f}) for fluorinated CB-filled low-density polyethylene (*LDPE*) composites

increasing fluorine content on the CB surface. Miyasaka and coworkers [3, 4] assumed that the interfacial energy between the polymer matrix and the CB particles acts as a driving force, and the CB particles begin to aggregate to form conductive networks if the interfacial energy between the CB particles and the polymer matrix reaches a critical value (Δg^*) and they suggested an equation as follows:

$$\frac{1}{V_{\mathrm{f}}*} = 1 + \frac{3K}{\Delta g * R}, \tag{6}$$

where R is the radius of the CB particle, and K is the interfacial energy [25] between the polymer matrix and the CB particle; the equation form is same as Eq. (3). From Eq. (6), we can expect that V_{f}^* increases with decreasing K. The relation between K and V_{f}^* in this study is presented in Table 3. From Table 3, we obtained the result that V_{f}^* increases with decreasing K. As known, the conductive paths of CB particles in an insulating polymer matrix either have physical contact between them or are separated by very small distances across which electrons can hop by tunneling. In the percolation region, i.e., the resistivity changes from insulator to conductor, the tunneling conductivity increases exponentially with a decrease in the separation of the gap between the CB particles [32, 33]; therefore, the resistivity of CB-filled composites is very difficult to control in the semiconductive region. Accordingly, such materials are expected to be a new class of conductive polymer composite materials for industry. As shown in Fig. 1, the percolation curve showed a gradually decreasing trend on increasing the fluorine content of the CB particle. The same phenomenon has been observed using poly(methyl metacrylate) (PMMA) [8] or high-density PE (HDPE)/isotactic polypropylene (iPP), HDPE/PMMA and iPP/PMMA immiscible polymer blends as a polymer matrix [9]. This phenomenon is due to the effect of the forming nonconductive C–F covalent bonds onto the CB surface caused by fluorination. The result of Fig. 1 clearly shows that the treatment of the surface of the CB particle by fluorine is effective in controlling the resistivity in the semiconductive region. However, the treatment causes the increase in V_{f}^* for CB-filled polymer composite systems, which is a disadvantage for holding down the cost from an industrial viewpoint. The disadvantage can be improved using an immiscible polymer blend as a matrix [9].

The effect of the chemical structure of the polymer matrix on percolation behavior

In this section, the effect of copolymerization of PE with a VA functional group on the dispersion state of CB0 is examined. The chemical structure of EVA is shown in Fig. 2, and the characteristics of the raw materials are given in Table 5. CB0 and EVA were mixed at 120 °C using a two-roll mill, and then the composite films were formed using a compression-molding method.

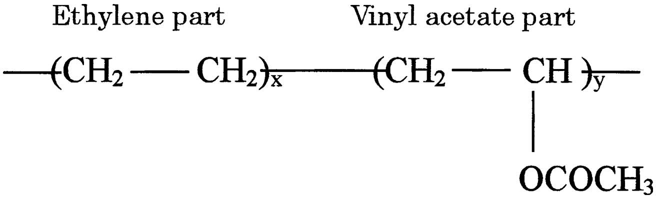
$$-(CH_2-CH_2)_x-(CH_2-\underset{OCOCH_3}{\underset{|}{CH}})_y-$$

Fig. 2 Chemical structure of poly(ethylene-*co*-vinyl acetate) (*EVA*)

Table 5 Characteristics of poly(ethylene-*co*-vinyl acetate) copolymers

	Vinyl acetate content (wt %)	Melt mass flow rate (g/10 min)	density (g/cm^3)
EVA-10	10	9	0.929
EVA-42	42	70	0.968

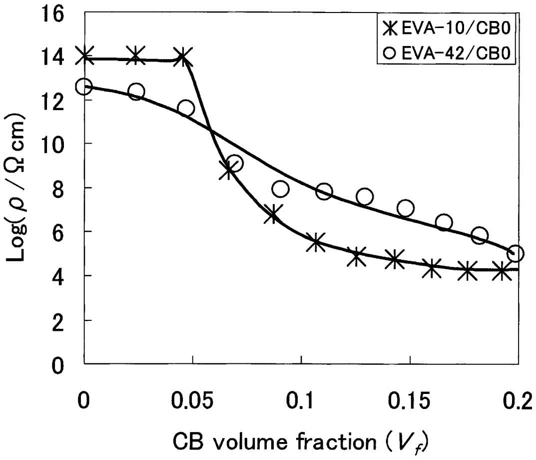

Fig. 3 Relationships between ρ and V_{f} for CB0-filled EVA composites

The effect of the volume fraction (V_{f}) on the volume resistivity (ρ) for the CB0-filled EVA composite at room temperature (25 °C) is depicted in Fig. 3. The value of ρ for the unfilled EVA-10 system is approximately 10^{14} Ω cm, while the unfilled EVA-42 system exhibits approximately 10^{12} Ω cm. It has been suggested that the decrease in ρ of EVA is due in part to the polar groups of the VA comonomer [18]. As shown in Fig. 3, although V_{f}^* for the EVA-10 system could be observed at $V_{\mathrm{f}}=0.05$ ($V_{\mathrm{f}}{}^*{}_{\mathrm{EVA\text{-}10/CB0}}=0.05$), V_{f}^* for the EVA-42 system could not be observed. Sumita et al. [4] have confirmed that the transition in resistivity from the insulating state to the conductive state in the relation between V_f and ρ become less clear on increasing the VA content for the CB-filled EVA systems when the VA content is more than 32 wt %. The disappearance of V_f* for CB-filled EVA systems is due to the decrease of V_f* by increasing K accompanied with increasing the VA content [4]. Moreover, it was found that the EVA-42/CB0 system has a broader percolation curve, and has a higher ρ for V_f above 0.05. This continuous decrease of ρ for the EVA-42 system suggests that the CB aggregation suddenly does not occur and a conductive CB network cannot be formed in the EVA-42 matrix. Previous works mentioned that these differences of the CB dispersion state in CB-filled EVA systems are ascribed to the polar attribute of EVA that often gives CB better wettability and dispersion in the polymer matrix [4, 16, 17, 18, 19]. From these results, it was suggested that the chemical modification of PE with a VA functional group is effective in controlling the resistivity in the semiconductive region for CB-filled polymer composites, as well as fluorination on the CB surface as shown in Fig. 1.

For better understanding of the dispersion state of CB particles in an EVA matrix, we obtained SEM photographs. The SEM photographs of the EVA-10/CB0 and EVA-42/CB0 systems containing CB particles of $V_f = 0.13$ are shown in Fig. 4. In this figure, the white points are CB particles in a polymer matrix. We can see the apparent difference in the dispersion state of the CB particles between the EVA-10 and EVA-42 systems. Moreover, we calculated the total surface area per unit mass of CB particles in the polymer matrix from SAXS measurements. SAXS measurement is known as an effective tool for a quantitative estimation of the dispersive state of filler particles [20, 23, 34, 35, 36, 37]. In such cases as a colloidal dispersive two-phase system, it is known generally that the total surface area of a unit mass of the dispersed phase, A (meters squared per gram), can be calculated in two ways. One was suggested by Porod [34, 35], and the other was suggested by Debye [36]. The Debye method is rapider than the Porod method both experimentally and computationally. However, it must be emphasized that the Debye method is confined to completely random system [36, 37]. Further, the method uses the intensity for only a few low-angles. Therefore, it is assumed that the Debye method is not suitable for such a system as CB-particle-filled polymer composites since CB particles are formed as agglomerates in the polymer matrix in the region above V_f*. On the other hand, the Porod method can be utilized when the system can be considered to be an ideal two-phase system; furthermore, the periodic structure does not exist in the system [37]. Accordingly, it is assumed that the Porod method is more suitable than the Debye method for such dense systems as those containing CB particles with V_f above V_f*. According to the method of Porod [34, 35, 37] at the tail (high-angle end) of the scattering curve, the scattered intensity should be proportional to $1/s^3$ for a two-phase system with the use of an infinite slit. Thus we have, at high angles (in the small-angle region),

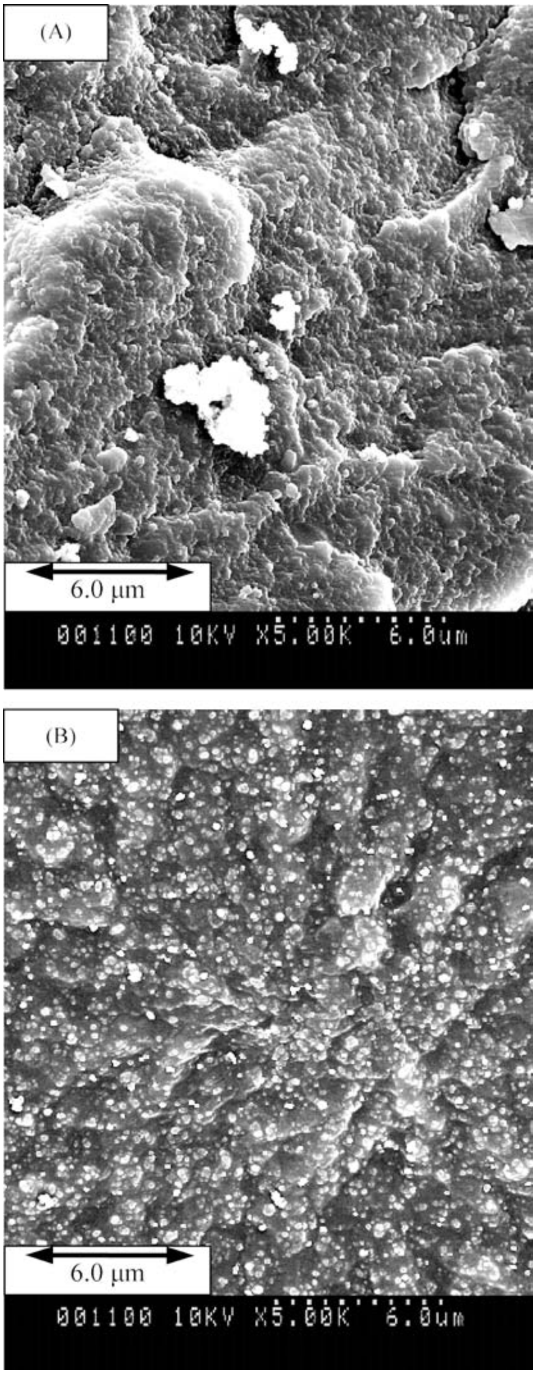

Fig. 4a, b Scanning electron microscopy photographs of CB0-filled EVA composite for $V_f = 0.13$. **a** EVA-10 filled with CB0; **b** EVA-42 filled with CB0

$$\tilde{I}(s) = k/s^3 \tag{7}$$

and

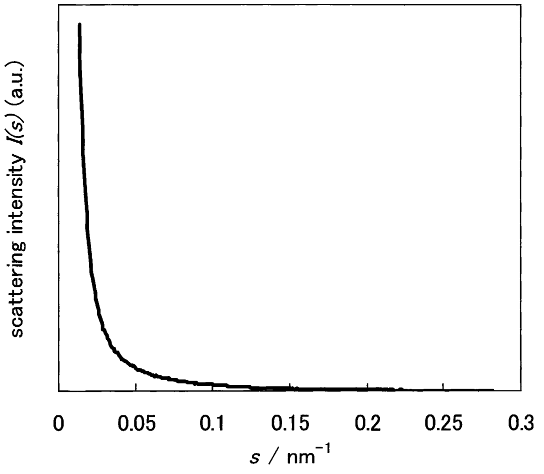

Fig. 5 Small-angle X-ray scattering profile for EVA-10 filled with CB0 containing $V_f = 0.05$

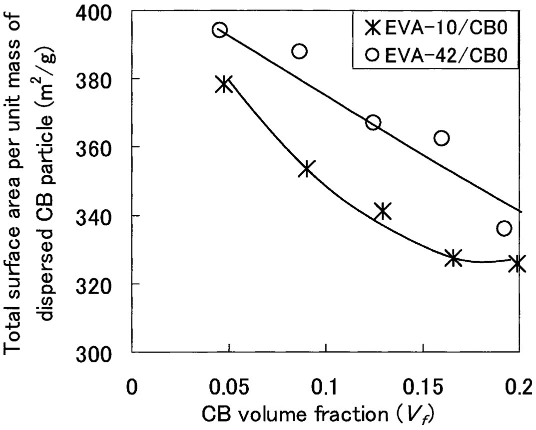

Fig. 6 Relationships between the total surface area per unit mass of dispersed CB particles and CB volume fraction for EVA filled with CB0 composites

$$s = \frac{2\sin\theta}{\lambda}, \tag{8}$$

where k is constant. In practice Porod's law is usually obeyed for $2\theta > 1$–$2°$. 2θ is the scattering angle, λ is the wavelength of the X-rays, and $\tilde{I}(s)$ is the scattering intensity measured by slit collimation. The total surface area of a unit mass of the dispersed phase, A, can be calculated from the equation as follows:

$$A = \frac{8\pi(1-\phi_1)}{d_1 Q_s} \lim_{s\to\infty}\left[s^3\tilde{I}(s)\right], \tag{9}$$

where ϕ_1 is the volume fraction and d_1 is the density of the filler. The invariant Q_s is obtained by appropriate integration of the experimental data:

$$Q_s = \int_0^{\infty} s\tilde{I}(s)\mathrm{d}s. \tag{10}$$

The raw data of the SAXS profile for EVA-10 filled with CB0 containing $V_f = 0.05$ are shown in Fig. 5. The diffraction patterns caused by the periodic structure in the SAXS profiles for all CB0-filled EVA systems are not shown in Fig. 5. The dependence of the surface area per unit mass of dispersed CB on V_f above the percolation threshold for CB0-filled EVA systems is shown in Fig. 6. As shown in Fig. 6, it was observed that the surface area of the CB0 particles decreased with increasing V_f. It follows from this result that the CB particles are aggregated by addition of CB particles. In the light of the decrease in ρ for EVA filled with CB0 as shown in Fig. 3, we can notice that the surface area decreased linearly, whereas ρ decreased exponentially, with an increase in V_f. That is, the exponential decrease in ρ is caused by a decrease in the gap distance of the CB particles accompanying the aggregation of CB particles. This phenomenon is comprehended by taking into consideration that the tunneling conductivity increases exponentially on decreasing the gap distance between CB particles linearly. In addition, it was found that the value of the surface area of CB-filled EVA-42 systems was higher than that of EVA-10 systems for every V_f, because CB particles are dispersed better in the EVA-42 matrix than in the EVA-10 one, as shown in the SEM photographs (Fig. 4). Moreover, it was found that the surface area of the EVA-42 system showed a broader decreasing trend compared with that of the EVA-10 system as well as the volume resistivity measurement. A consistent relation was found between the volume resistivity measurement and the surface area estimated from SAXS measurement. Therefore, it was suggested that the difference in the percolation curve is due to the difference in the dispersion state of the CB particles.

Conclusion

Immersion heat calorimetry had been used to characterize the surface of fluorinated CBs. From the results, the London dispersive component turned out to be the predominant factor of the surface energy of fluorinated CBs. Additionally, it was found that the London dispersive component of the surface energy significantly decreased, while the polar component slightly increased, and the total surface energy of the CB particles decreased with increasing surface fluorine content.

By volume resistivity measurements, it was found that the percolation threshold increased on fluorination of the CB particles because of decreasing interfacial free energy between the polymer matrix and the CB particles accompanied with a decrease in the surface energy of the CB particles. Moreover, the percolation curve became moderate on fluorination of the CB surface. It was shown that treatment of CB particles by fluorine is effective in controlling the resistivity in the semiconductive region although the treatment causes an increase in V_f* for CB-filled polymer composite systems. On the other hand, the percolation threshold was diminished and the percolation curve was moderated, by an increase in the VA content of the EVA used as a matrix. That is, it was suggested that copolymerization of PE with VA is effective in the design of semiconductive polymer composite materials as well as fluorination of the CB surface. From SAXS measurements, the total surface area per unit mass of dispersed CB particles in the EVA matrix decreased with increasing volume fraction of the CB particles. Moreover, it was found that the decrease in the surface area is moderated by an increase in the VA functional group content. A consistent relation was found between the volume resistivity measurement and the surface area estimated from SAXS measurement. It was suggested that the difference in the percolation curve is due to the difference in the dispersion state of the CB particles.

References

1. Buche FJ (1972) Appl Phys 43:4837
2. Buche FJ (1973) Appl Phys 44:532
3. Miyasaka K, Watanabe K, Jojima E, Aida H, Sumita M, Ishikawa K (1982) J Mater Sci 17:1610
4. Sumita M, Asai S, Miyadera N, Jojima E, Miyasaka K (1986) Colloid Polym Sci 264:212
5. Wessling B (1988) Synth Met 27:A83
6. Lux F (1993) J Mater Sci 28:285
7. Ando N, Takeuchi M (1998) Thin Solid Films 334:182
8. Wu G, Zhang C, Miura T, Asai S, Sumita M (2000) J Appl Polym Sci 80:1063
9. Katada A, Akiyama K, Isogai T, Tominaga Y, Asai S, Sumita M (2003) Mater Sci Technol 40:35
10. Katada A, Konishi Y, Isogai T, Tominaga Y, Asai S, Sumita M (2003) J Appl Polym Sci 89:1151
11. Katada A, Isogai T, Sumita M (2003) J Soc Rubber Ind 76: 375
12. Rodrigues J, Hamed GR (1996) Rubber Chem Technol 69:286
13. Katada A, Shimura S, Tominaga Y, Asai S, Sumita M (2004) J Appl Polym Sci 91:2928
14. Isogai T, Maruyama S, Yamana M, Kubo M (1994) In: Annual 21st meetings of the Carbon Society. Abstract 278
15. Isogai T, Yamaguchi F, Kubo M (1998) Fluorine in coatings III papers. The Paints Research Association 27
16. Shout TR, Moffatt D, Huebner W. (1991) J Mater Sci 26:145
17. Xiao Y, Wu G, Ma D (1998) J Appl Polym Sci 67:131
18. Zhang JF, Zheng Q, Yang YQ, Yi XS (2002) J Appl Polym Sci 83:3112
19. Park SJ, Kim HC, Kim HY (2002) J Colloid Interface Sci 255:145
20. Brown DS, Warner FP, Wetton RE (1972) Polymer 13:575
21. Young RJ, Al-khudhairy DH, Thomas AG (1986) J Mater Sci 21:1211
22. Deslandes Y, Whitemore MK, Bluhm TL, Hokansson A (1988) J Dispersion Sci Technol 9:235
23. Zhang C, Yi XS, Asai S, Sumita M (1999) Compos Interfaces 6:28
24. Brunauer S, Emmett PH, Teller E (1938) J Am Chem Soc 60:309
25. Owens DK, Wendt RC (1969) J Appl Polym Sci 13:1741
26. Schonhorn H (1966) Nature 210:896
27. Kraus G. (1955) J Phys Chem 59:343
28. Tsutsumi K, Abe K (1989) Colloid Interface Sci 267:637
29. Gonzalez-Martin ML, Junczuk B, Labajos-Broncano L, Bruque JM (1997) Langmuir 13:5991
30. London F (1937) Trans Faraday Soc 33:8
31. Fox HW, Zisman WA (1950) J Colloid Sci 5:514
32. Sichel EK (ed) (1982) Carbon black polymer composites. Dekker, New York
33. Ezquerra TA, Kulescza M, Balta Calleja FJ (1991) Synth Met 41:915
34. Porod VG (1951) Kolloid Z 124:83
35. Porod VG (1952) Kolloid Z 125:51
36. Debye P, Anderson HR, Brumberger H (1957) J Appl Phys 28:679
37. Dawkins JV (ed) (1978) Developments in polymer characterization-1. Applied Science, London