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ORIGINAL CONTRIBUTION

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Relationship between electrical resistivity and particle dispersion state for carbon black filled poly (ethylene-*co*-vinyl acetate)/poly (L-lactic acid) blend

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Abstract It is known that the electrical volume resistivity of insulating polymers filled with conductive fillers suddenly decreases at a certain content of filler. This phenomenon is called percolation. Therefore, it is known that controlling resistivity in the semi-conductive region for carbon black (CB) filled composites is very difficult. When poly (ethylene-co-vinyl acetate) (EVA) is used as a matrix, the percolation curve becomes gradual because CB particles disperse well in EVA. In this study, the relationship between the dispersion state of CB particles and electrical resistivity for EVA/poly (L-lactic acid) (PLLA) filled with CB composite was investigated. The apparent phase separation was seen in the SEM photograph. It was predicted that the CB particles located into the EVA phase in the light of thermodynamical consideration, which was estimated from the wetting coefficient between polymer matrix and CB particles. The total surface area per unit mass of dispersed CB particles in the polymer blend matrix was estimated from small-angle X-ray scattering and the volume resistivity decreased with increasing CB content. The values of the surface area of CB particles in CB filled EVA/PLLA (25/75 wt%) and EVA/PLLA (50/50 wt%) polymer blends showed a value similar to that of the CB filled EVA single polymer matrix. In electrical volume resistivity measurement, moreover, the slopes of percolation curves of EVA/PLLA (25/75 wt%) and EVA/PLLA (50/50 wt%) filled with CB composite are similar to that of EVA single polymer filled with CB composite. As a result, it was found that CB particles selectively locate in the EVA phase, and then the particle forms conductive networks similar to the networks in the case of EVA single polymer used as a matrix.

Keywords Polymer composite materials · Filler · Small-angle X-ray scattering (SAXS) · Poly(ethylene-*co*-vinyl acetate) (EVA) · Poly (L-lactic acid) (PLLA)

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 conductive particles content and the resistivity of composites implies some sudden change in the dispersion state of the conductive particles, i.e., the aggregation of the particles to form networks that facilitate the electrical conduction through the composite. This transition-like phenomenon is called the percolation phenomenon, and the critical CB volume fraction is called 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 transition-like behavior [1–6]. At the same time, the control of volume resistivity in the semi-conductive region, which ranges from 10^5 Ω cm to 10^8 Ω cm, for the CB filled polymer composite, is also an important subject from an industrial point of view. Therefore, a report on resistivity control in the semi-conductive region is very important as is the determination of V_f* for CB filled polymer composite systems [7–12].

Poly(ethylene-co-vinyl acetate) (EVA) has been noticed as a matrix for CB-filled polymer composite because the polarity and the surface energy of EVA can be changed by variations in the vinyl acetate (VA) content [4, 13, 14]. In particular, it has been reported that the percolation curve became gradual with an increase in VA content [4, 12]. This is caused by the nature of the dispersion state of CB particles, which is improved with an increase in VA content [12]. Previous works have mentioned that the dispersion state of CB particles in EVA is ascribed to the polar attribute of EVA that often puts CB into better wettability and dispersion in the polymer matrix [13, 14]. That is to say, the use of EVA as a polymer matrix is suitable for the design of semi-conductive polymer composites. However, EVA has low modulus at room temperature due to the glass transition temperature (T_g) of EVA being lower than room temperature. Consequently, it has a rubbery nature and hence EVA is not suitable for holding several forms. Incidentally, poly(L-lactic acid) (PLLA) can be utilized for both ecological and biomedical applications because of its biodegradable characteristic, though, its brittleness at room temperature is a major defect for many applications. In order to modify the mechanical property, many studies of PLLA blends with other polymers have been carried out [15–18]. In particular, PLLA/EVA blends have been reported by Yoon et al. [18] in terms of their miscibility and mechanical properties. The blends showed that the mechanical property, strain-at-break, improved by blending with EVA. When CB particles fill into such a polymer blend matrix, it has been suggested that CB particles locate in one phase, or interface between two polymers [19–24]. Both the conductive network of CB particles in the filler located phase and the continuity of this phase in the composites are basic requirements for maintaining a conductive network through the composite. This concept has been designated double percolation [19, 21, 23, 24].

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 [12, 25–29]. The main requirement is that there is a sufficient difference of electron density between the different phases for appreciable scattering of X-ray. The total surface area per unit mass of dispersed filler can be calculated from this measurement. However, little has been reported on the relation between the total surface area of dispersed CB particles and the percolation behavior of polymer blends filled with CB composite system [29].

The present work is focused on the interrelationship between the filler dispersion state and the electrical property of EVA/PLLA blend filled with CB composite by means of scanning electron micrograph (SEM), SAXS and electrical volume resistivity measurements.

Experimental

Materials

The raw materials used in this study were commercial products. Poly(ethylene-co-vinyl acetate) (EVA), that contains 42 wt% of vinyl acetate, was supplied from Tosoh Co. Japan. Poly(L-lactic acid) (PLLA) was supplied from Toyota Motor Co. Japan. The physical characteristics of these polymers are summarized in Table 1. Conductive carbon black (CB) particle supplied from Denki-kagaku Co. Japan was used. The particle diameter, density and BET surface area [30] of the particle is 42 nm, 1.95 g/cm^3 and 69 m^2/g, respectively.

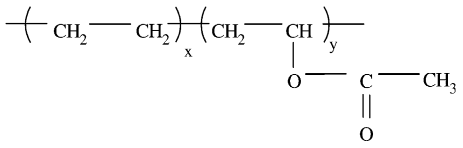
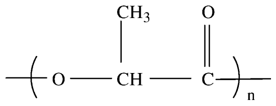
Preparation of the CB filled polymer composite film

The CB particles were dried at 110°C under vacuum overnight before mixing. The mixing of EVA/PLLA, EVA/CB and EVA/PLLA/CB was carried out at 180°C for 15 min using a two-roll mill (Nishimura machinery Co., Ltd). For the composite of EVA/PLLA/CB, the EVA was first mixed with PLLA at 180°C for 10 min followed by the addition of CB and then mixed for 5 min. Freestanding sheets with a thickness of about 0.4 mm were obtained from the mixtures by the compression molding method at 180°C for 10 min under a pressure of 19.6 MPa using a hot press (Technosupply Co. Ltd., Japan), followed by quenching in ice water.

Dynamic mechanical property

Mechanical property was estimated by means of dynamic mechanical analysis. It was carried out with IT-DVA 200S (ITK Co., Japan). For this measurement, the prepared freestanding sheets were cut into rectangular shapes (30×5 mm^2). This experiment was performed in a tension mode with 0.1% strain amplitude at a frequency

Table 1 Physical characteristics of polymers

Polymer	Structural formula	Density (g/cm^3)	Viscosity at 180°C[a] (Pa s)	Melt index (g/10 min)	Mw[b]
EVA	 $-\left(CH_2-CH_2\right)_x-\left(CH_2-\underset{O-\overset{\overset{O}{\|}}{C}-CH_3}{CH}\right)_y-$	0.968	300	70	–
PLLA	 $-\left(O-\overset{CH_3}{CH}-\overset{\overset{O}{\|}}{C}\right)_n-$	1.248	5,340	–	557,000

[a] Measured by dynamic rheological analyzer (Physica UDS200, Physica Messtechnik)
[b] Measured by Gel permeation chromatography (G. P. C.) [31] (Shodex RI-71)

of 1 Hz. The temperature ranged from −50°C to 100°C with a heating rate of 5°C/min.

Scanning electron microscopy (SEM) observation

The morphology of EVA/PLLA polymer blend and the dispersion of CB particles in polymer blend matrix were observed using a field-emission-type scanning electron microscopy (FE-SEM S800, HITACHI High-technologies Co.). Specimens were fractured in liquid nitrogen. The broken surface was then etched by Ar ion for 15 min using an Eiko IB-3 equipment and coated with Pt-Pd.

Small-angle X-ray scattering (SAXS) measurement

SAXS measurements were carried out using a Rigaku RU-200, working at 50 kV and 180 mA, with slit-collimated Cu-$K\alpha$ radiation of the wavelength of 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 placed just before the receiving slit.

Electrical volume resistivity measurement of CB filled polymer composite films

The electrical volume resistivity was measured using a Keithley 487 picoammeter (Keithley Instruments, Inc.) equipped with a direct current (DC) voltage source. The specimen (width×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 copper electrodes. The specimens were then placed in a temperature-controlled chamber. The volume resistivity measurements were performed in the thickness direction of the specimen by using a two-terminal method under DC condition at room temperature. The electrical volume resistivity (ρ) is calculated as follows,

$$\rho = R\frac{S}{t}, \tag{1}$$

where R is the volume resistance, S is the area and t is the thickness of specimen.

Results and discussion

Dispersion state of CB particles in EVA/PLLA blend matrix

Figure 1 shows the results of dynamic mechanical analysis, (a) shows the temperature dependency of storage modulus, E', and (b) shows the temperature dependency of mechanical loss tangent ($\tan\delta = E''/E'$) for EVA, PLLA and EVA/PLLA (50/50 wt%) blend. E'' is related to the dissipation energy by heating attributed to the deformation of the material and E' is a measure of recoverable strain energy in the deformed material. From Fig. 1a, it is obvious that E' at room temperature is improved by blending with PLLA. With regard to temperature dependence of tan δ for EVA in Fig. 1b, the tan δ peak at around −25°C corresponds to the glass transition temperature (T_g) of EVA. With regard to tan δ for PLLA, it is clear that the tan δ peak can be seen at around 60°C for PLLA in Fig. 1b. PLLA is crystalline polyester with a melting temperature (T_m) of around 170°C and a T_g of around 57°C [31]. It crazes easily since PLLA is very brittle at room temperature.

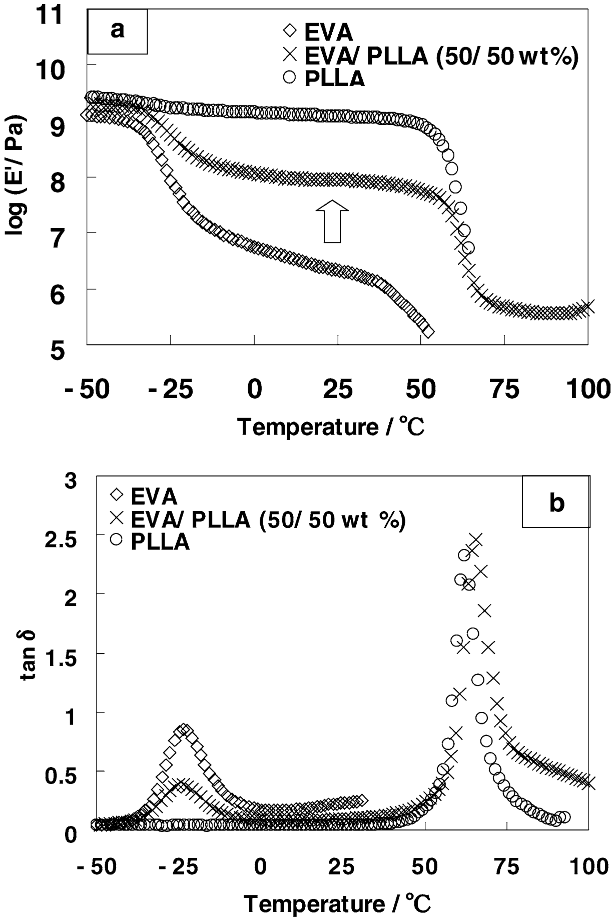


Fig. 1 Dynamic mechanical behavior of neat EVA, PLLA and EVA/PLLA (50/50 wt%) blend: **a** temperature dependence of storage modulus (E') **b** temperature dependence of mechanical loss tangent (tan δ)

Therefore, there are several approaches for producing PLLA-based materials with a broad range of properties and improved mechanical properties, e.g., strain-at-break. These approaches include copolymerization and blending with other kinds of polymers, such as poly(vinyl acetate) (PVA) [15], poly(ethylene oxide) (PEO) [16], poly(vinyl phenol) (PVph) [17], and EVA [18]. It has been reported that poly(vinyl acetate) (PVA) is miscible with PLLA since the carbonyl group of PLLA interacts with the α-hydrogen of vinyl acetate (VA) unit due to their proton-accepting and proton-donating properties, respectively [15]. Yoon et al. [18] have reported the miscibility of PLLA with EVA containing 70 and 85 wt% of VA unit estimated from the Flory-Higgins theory. From that estimation, it has been suggested that a blend consisting of PLLA and EVA containing 85 wt% of VA unit indicates thermodynamical miscibility since the interaction parameter (χ_{12}) was found to be –0.043, whereas a blend comprising PLLA and EVA containing 70 wt% of VA unit indicates immiscibility. Dynamic mechanical analysis can often be used to characterize the miscibility between two polymers [18]. For an immiscible polymer blend, generally, the tan δ versus temperature curve shows the presence of two separated tan δ peaks corresponding to T_g's of individual polymers. For a miscible polymer blend, the curve shows only a single peak between the transition temperatures of the polymers. From Fig. 1b, the two separate tan δ peaks corresponding to the transition peak of EVA and PLLA can be observed for the EVA/PLLA (50/50 wt%) blend. It follows from this result that a blend consisting of PLLA and EVA containing 42 wt% of VA unit is found to be immiscible at the point of molecular mobility. Figure 2 shows the SEM photograph of EVA/PLLA (50/50 wt%) polymer blend filled with a CB system containing a volume fraction of 0.05 in the blend matrix. The white points are CB particles. We can see here an apparent phase separation structure.

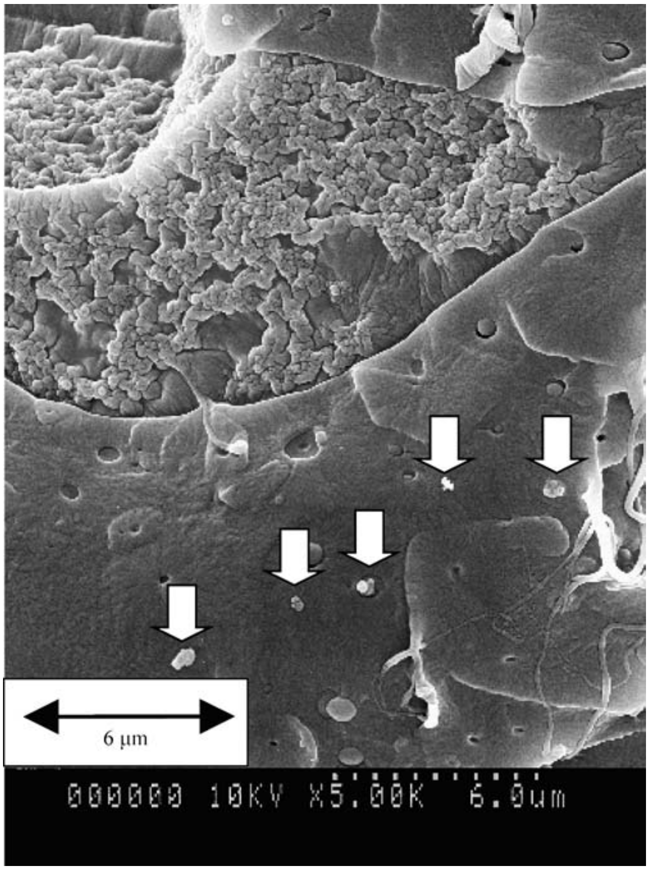


Fig. 2 SEM photograph of EVA/PLLA (50/50 wt%) polymer blend matrix filled with CB containing volume fraction of 0.05. *white arrows* indicate the CB particles

In the matrix of immiscible polymer blends, CB particles distribute unevenly to each component of the polymer blend. There are two types of distributions.

(1) One is predominantly distributed in one phase of the blend matrix. (2) In the second, the CB particle distribution concentrates at the interface of two polymers. Sumita et al. [19, 20] have suggested that the dispersion state of CB particles in polymer blend matrices can be predicted qualitatively from the value of the wetting coefficient, ω, which is defined as follows.

$$\omega_{A-B} = \frac{\gamma_{CB-B}\gamma_{CB-A}}{\gamma_{A-B}}, \tag{2}$$

where $\gamma_{i\text{-}j}$ is the interfacial energy between i phase and j phase. The $\gamma_{i\text{-}j}$ of each CB/polymer and polymer/polymer interface can be calculated using the values in Table 2. The following equation [32] was used.

$$\gamma_{i-j} = \gamma_i + \gamma_j - 2\sqrt{\gamma_i^{\mathrm{d}}\gamma_j^{\mathrm{d}}} - 2\sqrt{\gamma_i^{\mathrm{p}}\gamma_j^{\mathrm{p}}}. \tag{3}$$

For this calculation, the London dispersion component (γ^{d}), the polar component (γ^{p}) of surface energy and the total surface energy ($\gamma = \gamma^{\mathrm{d}} + \gamma^{\mathrm{p}}$) of each polymer and CB particle at molded temperature of 180°C are listed in Table 2. The values of γ^{d}, γ^{p} and γ of EVA, PLLA and CB were taken from the literature [11, 12, 33, 34], the values of EVA in Table 2 include 39 wt% of VA unit [33]. The values of surface energy of polymers at 180°C were obtained using the relation $\mathrm{d}\gamma/\mathrm{d}T = -0.06\ \mathrm{mJm^{-2}\ K^{-1}}$, which was the general value for polymers [34]. The value of surface energy of CB particles at 180°C was obtained using the relation: $\mathrm{d}\gamma/\mathrm{d}T = -0.07\ \mathrm{mJm^{-2}\ K^{-1}}$ [36, 37]. The next phenomenon has been predicted using Eqs. 2 and 3 [20]:

$\omega_{A-B} > 1$	CB particles locate in the A phase
$-1 < \omega_{A-B} < 1$	CB particles locate at the interface
$\omega_{A-B} < -1$	CB particles locate in the B phase

From these calculations, we obtained $\omega_{\text{EVA-PLLA}} = 2.69$. That is to say, it is predicted that CB particles are located in the EVA phase in light of the thermodynamical consideration. Moreover, in light of the chain mobility of several polymer phases, it is reasonable to suppose that CB particles are located in the EVA phase since CB particles tend to be located in the lower melt-viscosity phase [10] (see Table 1).

Table 2 Surface energy ($\gamma/\mathrm{mJm^{-2}}$) of EVA (containing 39 wt% of VA unit), PLLA and CB at 180°C. The values are taken from the literature indicated

	γ	γ^{d}	γ^{p}
EVA [33]	25.9	23.1	2.8
PLLA [34]	34.8	17.5	17.3
CB [11, 12]	108.8	108.1	0.7

Total surface area per unit mass of CB particles in the EVA/PLLA blend matrix estimated from Small angle X-ray scattering (SAXS) measurement

The SAXS measurement is known as an effective tool for the quantitative estimation of the dispersion state of filler particles [25–29]. In cases such as a colloid dispersion two-phase system, it is known generally that the total surface area of unit mass of dispersed phase, A ($\mathrm{m^2/g}$), can be calculated in two ways. One is suggested by Porod [38], and the other is suggested by Debye [39]. The advantage of the Debye method is that it is more rapid than the Porod method, experimentally and computationally. However, it must be emphasized that the Debye method is confined to completely random systems [26, 39]. Further, the method uses the intensity for only a few low angles [39]. Therefore, it is considered that the Debye method is not suitable for such systems as CB particle filled polymer composites since CB particles form agglomerates in a polymer matrix. On the other hand, the Porod method can be utilized when the system can be considered to be an ideal two-phase one, and the periodic structure does not exist in the system [26, 38]. Accordingly, the Porod method is more suitable than the Debye method for such dense systems as those containing CB particles of V_{f} above the percolation threshold (V_{f}*). According to the Porod method [26, 38], the scattered intensity at the tail (high angle end) of the scattering curve should be proportional to s^{-3} for a two-phase system in the use of a slit collimation. Thus we have, at high angles,

$$\tilde{\tilde{I}}(s) = k/s^3, \tag{4}$$

$$s = \frac{2\sin\theta}{\lambda}, \tag{5}$$

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

$$A = \frac{8\pi(1-\phi_1)}{d_1 Q_s} \lim_{s\to\infty}\left[s^3\tilde{\tilde{I}}(s)\right] \tag{6}$$

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

$$Q_s = \int_0^\infty s\,\tilde{\tilde{I}}(s)\mathrm{d}s \tag{7}$$

Guinier's law [40] was used for obtain $\tilde{\tilde{I}}(s)$ in the low-angle region, i.e., $s < 2\times10^{-2}\ \mathrm{nm^{-1}}$,

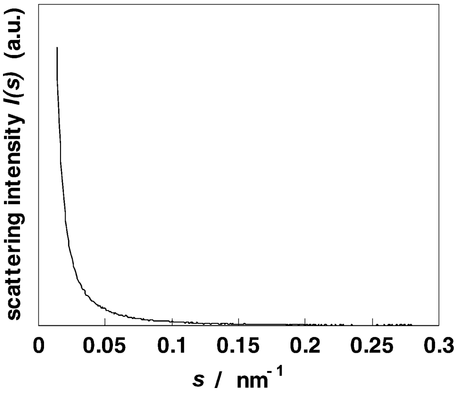


Fig. 3 Small-angle X-ray scattering (SAXS) profile for EVA/PLLA (50/50 wt%) polymer blend matrix filled with CB containing volume fraction of 0.05

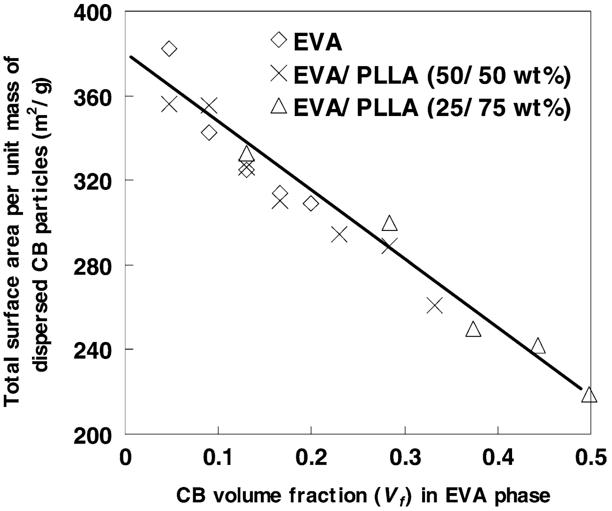


Fig. 4 Relationships between total surface area per unit mass of dispersed CB particles, A, (m^2/g) and CB volume fraction in EVA phase, V_f, for EVA, EVA/PLLA (25/75 wt%) and EVA/PLLA (50/50 wt%) blends

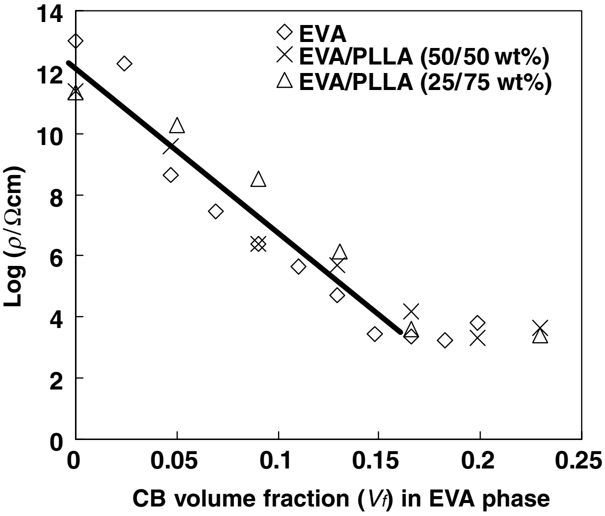


Fig. 5 Relationships between volume resistivity, ρ, and CB volume fraction in EVA phase, V_f, for EVA, EVA/PLLA (25/75 wt%) and EVA/PLLA (50/50 wt%) blends

$$\lim_{s\to 0}\tilde{\tilde{I}}(s) = \tilde{\tilde{I}}_0 \exp(C s^2), \qquad (8)$$

where $\tilde{\tilde{I}}_0$ is the scattering intensity at $s=0$, and C is constant.

Figure 3 shows the raw data of the SAXS profile for EVA/PLLA (50/50 wt%) polymer blend filled with CB containing volume fraction of 0.05. It does not show the diffraction patterns by the periodic structure in SAXS profiles for all CB filled systems as well as Fig. 3. Figure 4 shows the dependence of the total surface area per unit mass of dispersed CB volume fraction, V_f, for CB filled EVA, EVA/PLLA (25/75 wt%) and EVA/PLLA (50/50 wt%) systems. In particular, V_f shows the volume fraction of CB in the EVA phase because CB particles are located in the EVA phase estimated from the thermodynamical consideration (see below). As shown in Fig. 4, it was observed that the surface area of CB particles decreased with increasing V_f. It follows from this result that the CB particles are aggregated to each other by the addition of CB particles. Moreover, it is obvious that the total surface area of CB particles shows almost the same values for all composites, i.e., EVA, EVA/PLLA (25/75 wt%) and EVA/PLLA (50/50 wt%) blends filled with CB of same volume fraction. This fact supports that CB particles locate in the EVA phase, and thus the CB particles aggregate together in the EVA phase with an increase in V_f, for all samples.

Percolation behavior of CB filled EVA and EVA/PLLA blends

The effect of V_f on volume resistivity (ρ) for CB filled EVA, EVA/PLLA (50/50 wt%) and EVA/PLLA (25/75 wt%) composite systems at room temperature is depicted in Fig. 5. V_f shows the volume fraction of CB in the EVA phase. The value of ρ for an unfilled EVA system is approximately 10^{13} Ω cm, while a PLLA blend system exhibits approximately 10^{11} Ω cm. Jachym [41] has pointed out that long-chain polymers containing covalent bonds in the carbon skeleton, sufficiently strong to form wide bands, should have conductivity characteristics typical of semi-conductors. As a consequence of the slight intermolecular orbital overlapping, the electrons and holes are formed to move in close proximity to the chain. This explains the small electron conductivity of polymers, which have polar functional groups, such as the carbonyl group. The carbonyl group of PLLA interacts with the α-hydrogen of the VA unit due to their proton-accepting and proton-donating properties [15], and thus the conductivity is increased by blending with PLLA.

In the light of the decrease in ρ for EVA, EVA/PLLA blends filled with CB systems as shown in Fig. 5, we can see that the surface area decreases linearly (see Fig. 4), whereas ρ decreases exponentially with increase in V_f. The exponentially 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 understanding that the tunneling conductivity increases exponentially by decreasing the gap distance between CB particles in the polymer matrix [41, 42]. It is well known that the selective location of CB particles in one phase of a separated two-phase polymer causes a decrease of the percolation threshold, V_f*, to a very low level [23, 24]. The electrical properties of such composites strongly depend on the phase morphology. Both the conductive network of CB particle in the filler located phase and the continuity of this phase in the composites are basic requirements for maintaining a conductive network through the composite. This has been designated as the concept of double percolation [19, 23, 24]. Gubbels et al. [24] have examined the continuity of polymer phase in PE/polystyrene (PS) polymer blends in the presence of CB particles. It has been suggested that the required dual phase continuity can be reached with as small as 5 wt% of PE for the investigated PE/PS polymer blend. Hence, it seemed reasonable to think that 25 wt% of EVA is sufficient to form the continuous phase in the CB filled EVA/PLLA polymer blend system. Incidentally, Asai [19, 22] has pointed out that in the case of CB locating into one phase, the ρ of CB filled immiscible polymer matrix corresponds to that of CB filled single polymer matrix when V_f is converted in volume fraction in the phase in which CB particles are located. As shown in Fig. 5, the slopes of decreasing curves of ρ for CB filled EVA/PLLA (25/75 wt%) and EVA/PLLA (50/50 wt%) blends are the same as EVA filled with CB composite. This fact suggests that CB particles selectively locate in the EVA phase, and that the particles then form conductive networks similar to the networks seen when the EVA single polymer used as matrix.

Conclusion

DMA results showed that storage modulus, E', at room temperature was increased by blending with PLLA, and two separated glass transition peaks on temperature dependency of tan δ curve for EVA/PLLA (50/50 wt%) blend were seen. This result suggests that EVA and PLLA form an immiscible polymer blend. An apparent phase separation structure between EVA and PLLA in CB filled EVA/PLLA (50/50 wt%) blend was seen in the SEM photograph. From the calculation of wetting coefficient, ω, between the polymer and CB, it was decided that CB particles are located in the EVA phase in the light of thermodynamical considerations.

The total surface area per unit mass of dispersed CB particles in the EVA, EVA/PLLA (25/75 wt%) and EVA/PLLA (50/50 wt%) polymer blend matrix was estimated from SAXS measurement. The surface area of CB is decreased linearly, whereas ρ is decreased exponentially, with increasing V_f of the CB particle. A consistent relation was found between the volume resistivity measurement and the surface area of CB particles in polymer composites estimated from SAXS measurement. Moreover, the values of the surface area of CB and ρ for CB filled EVA/PLLA immiscible polymer blend showed similar to those of CB filled EVA single-polymer composites. It follows from this result that CB particles selectively locate in the EVA phase, and then the particle forms conductive networks in the EVA/PLLA blend matrix similar to the networks in the EVA single-polymer matrix. This fact suggests that the dispersion state of CB particles is similar to CB filled in single polymer matrix in cases where CB particles are located in one phase.

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